





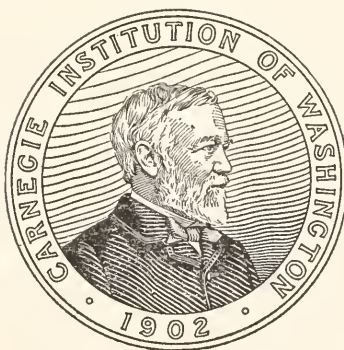




# THE GASES IN ROCKS

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# THE GASES IN ROCKS.

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It has been known for a long time from microscopical studies that some minerals inclose minute cavities which contain both liquid and gaseous matter. For a much shorter period it has been known that various igneous rocks, when exposed to red heat in a vacuum, evolve several times their volume of gas of quite variable composition. Since these gases occur in proportions entirely different from those of the constituents of the air, it has not seemed probable that they were derived directly from our present atmosphere, unless the rocks manifest some power of selective absorption not now understood. The apparent difficulties involved in this conception have suggested that some earlier atmosphere was rich in those gases. This involves a hypothesis relative to the changes through which the atmosphere has passed, and leads on to a theory of its origin and that of the earth itself. An alternative hypothesis regards these gases, not as the products absorbed by a molten earth from its surrounding gaseous envelope, but as entrapped in the body of the earth during its supposed accretion, and hence that they are a source from which accessions to our present atmosphere might be derived.

A study of these gases in the rocks has seemed, therefore, to give promise of results of some value to atmospheric problems and, perhaps, to those of cosmogony. Because of this, it appeared advisable to determine more widely the range and the distribution of these gases, their relations to other geologic phenomena, and the states in which the gases, or gas-producing substances, exist in the rocks. The desirability of supplementary work will become more evident when it is noted that, while a considerable number of investigators have analyzed the gases in rocks, as will appear in the following historical statement, nearly all have contented themselves with a few determinations, and that even a full compilation of all such results leaves much to be desired from a geological point of view.

## HISTORICAL SKETCH.

As early as 1818 the attention of Sir David Brewster was called to the subject of inclosed water by the explosion of a crystal of topaz when heated to redness; but his studies were not published until 1826. In the mean time, Sir Humphry Davy opened the cavities in a few crystals and examined chemically the imprisoned liquid and gas.<sup>1</sup> Piercing a cavity in several cases suddenly caused the inclosed gas-bubble to contract to from one-sixth to one-tenth of its original volume. The gas was thought to be pure nitrogen. The basaltic rock from the neighborhood of Vicence con-

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<sup>1</sup> Sir Humphry Davy, *Phil. Trans.* 1822, Pt. II, pp. 367-376; *Ann. de Chim. et Phys.*, t. 21 (1822), pp. 132-143.

tained gas (supposedly nitrogen) in a still more rarefied state, as its density was 60 to 70 times less than that of the atmospheric air. Upon perforating a cavity in a quartz crystal from Dauphiné, an almost perfect vacuum was discovered. Davy regarded the rarefied condition of the inclusions in the crystals as strong evidence that the waters and gases did not penetrate the crystals at ordinary temperatures and pressures. This he believed a decisive argument in favor of the Huttonian, or Plutonian, school. However, a crystal from Brazil gave a very different result; an immediate expansion to a volume 10 to 12 times greater than the original followed the opening of a cavity. The composition of the gas was not determined. The existence of compressed gas in the same sort of cavities seems adverse to the conclusions which Davy based upon his earlier experiments, but he sought to explain the difference by supposing the crust to have been formed under a pressure more than sufficient to balance the expansion due to the heat.

Brewster<sup>1</sup> attacked the problem by observing the temperature at which the inclosed liquid passed over into the gaseous state. A number of tests showed this to range from 74° to 84° F. When raised to this temperature the vacuity always reappeared. Brewster interpreted as follows:

The existence of a fluid which entirely fills the cavities of crystals at a temperature varying from 74° to 84° may be held as a proof that these crystals were formed at the ordinary temperature of the atmosphere.

For thirty years after Brewster the field was neglected until, in 1858, Simmler<sup>2</sup> reviewed Brewster's work in the light of advancing scientific knowledge. Studying the liquid inclusions in quartz, topaz, amethyst, garnet, and other minerals, he arrived at the conclusion that the power of expansion of the liquid in these inclusions showed it to be carbon dioxide. Some years later Sorby, continuing the researches along the lines suggested by Brewster and Simmler, found that the amount of expansion of liquid carbon dioxide from 0° C. to 30° C. corresponded closely to that observed in the liquid of the sapphires with which he experimented.<sup>3</sup> In these sapphires it was noted that the liquid disappeared when warmed to approximately 30° C. As the critical temperature for carbon dioxide, above which no amount of pressure will condense it to a liquid, is 30.92° C. (87.7° F.), there remained little room for doubt that the gas was largely carbon dioxide. Sorby remarked that this gas "might have been inclosed, either as a highly dilated liquid or as a highly compressed gas; but since the other<sup>4</sup> liquid has deposited crystals which dissolve on the application of heat, it seems most probable that the water was caught up in a liquid state, sometimes, perhaps, holding a considerable amount of carbon dioxide in solution as a gas."

In the same year Vogelsang and Geissler<sup>5</sup> heated quartz crystals and, passing an electric spark through the gas thus liberated, examined its

<sup>1</sup> Sir David Brewster, *Trans. Roy. Soc. Edinburgh*, vol. 10 (1826), pp. 1-41; *Edin. Jour. of Science*, vol. 6, pp. 153-156.

<sup>2</sup> R. T. Simmler, *Pogg. Ann.*, vol. 105 (1858), pp. 460-466.

<sup>3</sup> H. C. Sorby and P. J. Butler, *Proc. Roy. Soc.*, vol. 17 (1869), pp. 291-303. Earlier papers by Sorby appeared as follows: *Phil. Mag.*, 4th series, vol. 15, p. 152; *Quart. Jour. Geol. Soc.*, vol. 14 (1858), p. 453; *Proc. Roy. Soc.*, vol. 13 (1864), p. 333.

<sup>4</sup> Saline water.

<sup>5</sup> Vogelsang and Geissler, *Pogg. Ann.*, vol. 137 (1869), pp. 56-75.



spectrum, which was found to show the presence of much carbon dioxide, together with water and a very weak trace of hydrogen. The presence of the hydrogen line, however, the authors were inclined to attribute to water-vapor.

Further researches upon the critical point of the gas in mineral cavities, carried on by Hartley,<sup>1</sup> yielded results varying from 26° to 34° C. The lowering of the temperature he ascribed to the presence of some incondensable gas, perhaps nitrogen, while he believed that the raising of the critical point observed in some of the quartz specimens was due to hydrochloric acid.

Forster<sup>2</sup> and Hawes<sup>3</sup> investigated smoky quartz, the former distilling from the Tiefengletscher crystals a brown fluid of an empyreumatic odor, giving reactions for ammonia and carbonic acid, from which he concluded that the coloring matter of smoky quartz was due to a nitrogenous hydrocarbon, decomposable by heat; the latter made a microscopic study of the liquid carbon dioxide in the bubbles of the cavities.

Investigations which have opened up a broader field were begun by Graham<sup>4</sup> in 1867 upon the Lenarto meteoric iron. By submitting a strip of the iron to a red heat in a vacuum for 35 minutes he obtained 5.38 cubic centimeters of gas from 5.78 cubic centimeters of the metal. Heated for an additional 100 minutes, there were evolved 9.52 cubic centimeters of gas having the following composition: H<sub>2</sub>, 85.68; CO, 4.46; CO<sub>2</sub>, none; N<sub>2</sub>, 9.86.

As this meteorite yielded about three times its volume of gas, and since "it has been found difficult, on trial, to impregnate malleable iron with more than an equal volume of hydrogen, under the pressure of our atmosphere," Graham drew the inference that this meteorite came from a body having a dense atmosphere of hydrogen gas. By the same process Mallet<sup>5</sup> extracted 3.17 volumes of gas from a Virginia meteorite. His results were in accordance with those of Graham: H<sub>2</sub>, 35.83; CO, 38.33; CO<sub>2</sub>, 9.75; N<sub>2</sub>, 16.09.

Wöhler<sup>6</sup> heated to redness some of the metallic granules from the iron basalt of Ovivak, Greenland, obtaining more than 100 volumes of gas which burned with a bluish flame (mostly carbon monoxide mixed with a little of the dioxide). His results, however, were vitiated by having used an iron combustion tube.

Pursuing the method adopted by Graham and Mallet, A. W. Wright<sup>7</sup> conducted a series of experiments on meteorites, which have remained to the present day the source of most of our knowledge of the gas content of these interesting bodies. Wright's chief contribution lies in his two tables showing that there is a marked difference between the gas contents of the iron and stony types of meteorites; for while, in the former, hydrogen is

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<sup>1</sup> W. N. Hartley, *Jour. Chem. Soc.* (1876), vol. 2, pp. 237-250.

<sup>2</sup> A. Forster, *Pogg. Ann.*, 143 (1871), pp. 173-194.

<sup>3</sup> G. W. Hawes, *Am. Jour. Science*, vol. 21 (1881), pp. 203-209.

<sup>4</sup> Thos. Graham, *Proc. Roy. Soc.*, vol. 15 (1867), p. 502.

<sup>5</sup> J. W. Mallet, *Proc. Roy. Soc.*, vol. 20 (1872), pp. 365-370.

<sup>6</sup> F. Wöhler, *Pogg. Ann.*, 146 (1872), pp. 297-302.

<sup>7</sup> A. W. Wright, *Am. Jour. Science*, vol. 9 (1875), pp. 294-302 and 459-460; vol. 11 (1876), pp. 253-262; vol. 12 (1876), pp. 165-176.

the most abundant gas, carbon dioxide is the most characteristic constituent of the latter. His analyses are given in table 1.

TABLE 1.

Meteorite.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Vol.
Iron meteorites:						
Tazewell County, Tenn.....	14.40	41.23	....	42.66	1.71	3.17
Shingle Springs, Cal.....	13.64	12.47	....	68.81	5.08	0.97
Arva, Hungary.....	12.56	67.71	....	18.19	1.54	47.13
Texas.....	8.59	14.62	....	76.79	....	1.29
Dickson County, Tenn. ....	13.30	15.30	....	71.40	....	2.2
Stony meteorites:						
Guernsey, Ohio.....	59.88	4.40	2.05	31.89	1.78	2.99
Pultusk, Poland.....	60.29	4.35	3.61	29.50	2.25	1.75
Parnallee, India.....	81.02	1.74	2.08	13.59	1.57	2.63
Weston, Conn. ....	80.78	2.20	1.63	13.06	2.33	3.49
Iowa County, Ia.....	35.44	1.80	0.0	57.88	4.88	2.50

This table shows that in the iron meteorites carbon dioxide in no case constituted more than 15 per cent of the gas evolved, while in every case but one the quantity of carbon monoxide was considerably greater. In the stony meteorites carbon monoxide is low, while carbon dioxide is, in the majority of analyses, much the most abundant gas. Hydrogen is more important in the iron meteorites than in the stony.

The same experimenter determined also the gases given off by the same meteorite at different temperatures. His figures for the Iowa County meteorite are shown in table 2.

TABLE 2.

Gas.	At 100°.	At 250°.	Below red heat.	At low red heat.	At full red heat.
Carbon dioxide .....	95.46	92.32	42.27	35.82	5.56
Carbon monoxide.....	.00	1.82	5.11	0.49	0.00
Hydrogen .....	4.54	5.86	48.06	58.51	87.53
Nitrogen .....	0.00	0.00	4.56	5.18	6.91
Total.....	100.00	100.00	100.00	100.00	100.00

The progressive decrease in the percentage of carbon dioxide and the corresponding increase of hydrogen with the elevation of the temperature are striking. His inquiries into other phases of the problem will be deferred until the discussion of principles, where it will be possible to treat each factor to better advantage, in its proper relation to the whole subject.

Several years later Wright applied his method of gas extraction and reliable quantitative analysis to the gases in smoky quartz,<sup>1</sup> which heretofore had been subjected chiefly to qualitative microscopical studies. However, only one determination was made—that of a crystal from Branchville, Connecticut, which yielded a small quantity of gas of the following composition: Carbon dioxide, 98.33; nitrogen, 1.67; hydrogen sulphide, sulphur dioxide, ammonia, fluorine, and chlorine, trace.

<sup>1</sup> Wright, Am. Jour. Science, vol. 21 (1881), pp. 209–216.

Wright regarded the fluorine and chlorine as being combined, and the ammonia as probably existing together with some of the carbon dioxide in the form of ammonium carbonate. The amount of water obtained, calculated as vapor, was slightly more than twice the volume of carbon dioxide.

Following Wright, Sir James Dewar,<sup>1</sup> in collaboration with Mr. Ansdell, made several more analyses of the meteoritic gases, and then, in an endeavor to discover the source and significance of these gases, directed a series of experiments upon the theory that graphite might be the retentive or generative constituent. Their analyses of the gases from graphites and from the matrix from which graphites have come revealed moderately high volumes.

TABLE 3.

Material.	Sp. gr.	Vol.	CO <sub>2</sub> .	CO.	H <sub>2</sub> .	CH <sub>4</sub> .	N <sub>2</sub> .
Celestial graphite. ....	2.26	7.25	91.81	....	2.50	5.40	0.1
Borrodale graphite. ....	2.86	2.60	36.40	7.77	22.2	26.11	6.66
Siberian graphite. ....	2.05	2.55	57.41	6.16	10.25	20.83	4.16
Ceylon graphite. ....	2.25	0.22	66.60	14.80	7.40	3.70	4.50
Unknown graphite. ....	1.64	7.26	50.79	3.16	2.50	39.53	3.49
Gneiss. ....	2.45	5.32	82.38	2.38	13.61	0.47	1.20
Feldspar. ....	2.59	1.27	94.72	0.81	2.21	0.61	1.40

Because the quantity of gas yielded by these specimens of graphite was so considerable, Dewar proceeded to ascertain whether graphite could absorb the different gases when allowed to stand in each of them for 12 hours. His experiments with the celestial graphite which had previously been deprived of its gases indicated that little or no absorption had taken place. "It is therefore evident," says Dewar, "that the large quantities of gas occluded in celestial meteorites can not be explained by any special absorptive power of this variety of carbon." Attempts to split up the hydrogen-producing compound with strong nitric acid and also to wash out, with ether, the possible carbonaceous source of the methane, appeared to show that the hydrogen existed in a very stable compound, and that, while the ether lessened the quantity of methane which the graphite afterwards furnished, it did not dissolve out all the carbonaceous compounds present, or else that the marsh-gas was subsequently formed during the heating of the material.

Dewar's analyses of gases from stony meteorites, which are in accord with Wright's results, are given in table 4.

TABLE 4.

Meteorite.	Sp. gr.	Vol.	CO <sub>2</sub> .	CO.	H <sub>2</sub> .	CH <sub>4</sub> .	N <sub>2</sub> .
Dhurmsala, India. ....	3.175	2.51	63.15	1.31	28.48	3.9	1.31
Pultusk. ....	3.718	3.54	66.12	5.40	18.14	7.65	2.69
Mocs. ....	3.67	1.94	64.50	3.90	22.94	4.41	3.67
Pumice stone. ....	2.50	0.55	39.50	18.50	25.4	....	16.60

An analysis of the gas extracted from the Orgueil meteorite revealed much sulphur dioxide, which Professor Dewar believed to have been derived

<sup>1</sup> Dewar and Ansdell, Proc. Roy. Inst., vol. 11 (1884-1886), p. 332 and pp. 541-552.

from the decomposition of sulphate of iron. In all, 57.87 volumes were obtained:  $\text{CO}_2$ , 12.77;  $\text{CO}$ , 1.96;  $\text{CH}_4$ , 1.50;  $\text{N}_2$ , 0.56;  $\text{SO}_2$ , 83. Leaving out the  $\text{SO}_2$ , 9.8 volumes remain, as follows:  $\text{CO}_2$ , 76.05;  $\text{CO}$ , 11.67;  $\text{CH}_4$ , 8.93;  $\text{N}_2$ , 3.33. This analysis, the most remarkable of the series, though Dewar does not mention the fact, shows a complete absence of hydrogen (an uncommon phenomenon), while the percentage of marsh-gas is unusually high. There is, however, reason to suspect that there was hydrogen liberated, but that it was oxidized to water by the action of the iron compound, following the decomposition of the sulphate.

In 1888 W. F. Hillebrand<sup>1</sup> discovered that the mineral uraninite when treated with acids slowly disengaged bubbles of gas. As the result of a well-selected series of tests this appeared, in the light of the chemical knowledge of that day, to be nitrogen. Trials with different varieties of the mineral revealed a rather significant relation between the percentage of uranyl and this gas. The greater the amount of the oxide, the more gas obtained.

Several years later, Sir William Ramsay's scepticism was aroused when his attention was called to the paper by Hillebrand, for he hesitated to believe that free nitrogen could be produced by treating any substance with sulphuric acid. To test the case, he decomposed cleveite with this acid, obtaining little nitrogen, but some 20 cubic centimeters of argon, which the spectroscope showed to be mixed with some other gas.<sup>2</sup> A brilliant yellow line which appeared in this spectrum coincided exactly with  $\text{D}_3$ , the so-called "helium" line, first discovered in the spectrum of the chromosphere of the sun by Sir Norman Lockyer in 1868. This was the first real acquaintance with helium, until then known only as a hypothetical substance existing in the sun. Lockyer immediately became interested in this discovery of helium in a terrestrial mineral, and attempted to prove that it was not a single gas, but a compound or a mixture of gases, basing his contention upon various strange lines in the spectrum.<sup>3</sup>

Ramsay, continuing his study of the gas from cleveite, perceived what had been previously overlooked, namely, that hydrogen generally was more abundant than helium—in one case amounting to 80 per cent of the total gas. The hypothesis that this hydrogen might have been formed by the breaking up of an unstable hydride, the form in which Ramsay thought the helium should be evolved, if it were derived from combination with the uranium or yttrium of the mineral, was put to the test, with the result that the evidence pointed strongly against the theory.<sup>4</sup> A series of minerals powdered and fused with potassium acid sulphate were found to yield gas, sometimes helium,<sup>5</sup> but oftener hydrogen and the oxides of carbon.<sup>6</sup>

In 1896 W. A. Tilden made an attempt to determine the condition in which helium and the associated gases exist in minerals. Argon and helium were of particular interest, for Tilden believed that these two elements will

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<sup>1</sup> W. F. Hillebrand, *Bull. U. S. G. S.*, pp. 43-79.

<sup>2</sup> Sir William Ramsay, *Proc. Roy. Soc.*, vol. 58 (1895), pp. 65-67.

<sup>3</sup> Sir J. N. Lockyer, a series of six short papers in *Proc. Roy. Soc.*, vols. 58, 59, and 60.

<sup>4</sup> Ramsay, *Proc. Roy. Soc.*, vol. 58, pp. 81-89.

<sup>5</sup> Ramsay, *Proc. Roy. Soc.*, vol. 59, pp. 325-330.

<sup>6</sup> Ramsay and Travers, *Proc. Roy. Soc.*, vol. 60, pp. 442-448.



not be found to enter into combination at such temperatures as are ordinarily attainable. In his own words:

It also appears improbable that in the minerals from which the mixture of gases containing helium has been extracted this element exists in a state of ordinary chemical combination, for, on treating the mineral with acids, no compound of helium with hydrogen has yet been observed, and the components of the minerals are of a kind which are commonly regarded as chemically saturated.<sup>1</sup>

The minerals monazite and cleveite were found to yield gas at low temperatures (60° and 110°, respectively), carbon dioxide appearing first. The monazite heated to 130° to 140° gave gas which, for the first time, showed the D<sub>3</sub> line, indicating the presence of helium. Between 140° and 250° there was obtained carbon dioxide with about one-fourth of its volume of a gas rich in helium. At higher temperatures up to 446° (boiling sulphur) there was less gas evolved. Cleveite behaved in a similar way. Studies on the absorption of helium by cleveite demonstrated that the mineral does not absorb this gas at the ordinary pressure, although placed in a helium atmosphere for nine weeks. But under pressure of 2.5 and 7 atmospheres, Tilden believed that he obtained an appreciable absorption. A trial with the Peterhead granite, which contained no helium in the first place, proved that the granite would absorb none of the gas whatever, even aided by a pressure of 7 atmospheres.

The finding of hydrogen as well as carbon dioxide in this Peterhead granite<sup>2</sup> led Tilden to investigate the gases inclosed in crystalline rocks.<sup>3</sup> His five complete analyses are as given in table 5.

TABLE 5.

Rock.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .
Granite, Skye.....	23.60	6.45	3.02	61.68	5.13
Gabbro, Lizard.....	5.50	2.16	2.03	88.42	1.90
Pyroxene gneiss, Ceylon.....	77.72	8.06	0.56	12.49	1.16
Gneiss, Seringapatam.....	31.62	5.36	0.51	61.93	0.56
Basalt, Antrim.....	32.08	20.08	10.00	36.15	1.61

In addition to these analyses, 25 carbon-dioxide determinations were made.

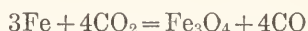
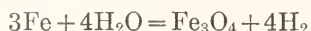
Tilden believed the gas to be "wholly inclosed in cavities which are visible in thin sections of the rock when viewed under the microscope. \* \* \* To account for the large proportion of hydrogen and carbon dioxide in these gases, it is only necessary to suppose that the rock inclosing them was crystallized in an atmosphere rich in carbon dioxide and steam, which had been, or were at the same time, in contact with some easily oxidizable substance, at a moderately high temperature. Of the substances capable of so acting, carbon, a metal, or a protoxide of a metal present themselves as the most probable." Hydrogen and carbon monox-

<sup>1</sup> W. A. Tilden, Proc. Roy. Soc., vol. 59 (1896), p. 218.

<sup>2</sup> Wright's two analyses, showing that trap rocks yield much the same gases as meteorites, also served to call attention to this field for investigation.

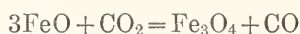
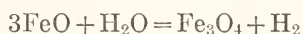
<sup>3</sup> Tilden, Chem. News, vol. 75 (1897), pp. 169-170.

ide might then be produced by the reducing action of metallic iron or ferrous oxide upon steam and carbon dioxide at high temperature, according to the reactions—



The origin of the marsh-gas is assigned in this paper to the action of water at high temperature upon metallic carbides, or similar compounds, in the earth's interior, as suggested by Mendeléef<sup>1</sup> and the more recent studies of Moissan.<sup>2</sup>

A year after the publication of Tilden's article, criticism of his paper, and in fact of the work of all previous investigators in this line, was made by M. W. Travers, who undertook to prove that the different gases, not excluding even argon and helium, did not exist in the gaseous state in minerals, but were formed by chemical interaction between the non-gaseous materials in the combustion-tube.<sup>3</sup> The key to his position lay in the two reversible reactions—



His table revealed a certain relation between the hydrogen and carbon monoxide produced, and the quantity of ferrous oxide and water present in the mineral. It is shown in table 6. The figures for FeO and H<sub>2</sub>O refer to the percentages in the rock; the gases are expressed in cubic centimeters per gram of rock.

TABLE 6.

Mineral.	FeO.	H <sub>2</sub> O.	H <sub>2</sub> .	CO.	CO <sub>2</sub> .
Chlorite, Moravia .....	10.6	4.6	2.180	0.494	0.123
Serpentine, Zermatt .....	2.7	9.5	0.800	None.	None.
Gabbro, Isle of Skye .....	6.1	1.5	0.490	None.	None.
Mica, Westchester, Pa. ....	1.4	0.13	....	0.08	0.150
Foliated talc, Tyrol .....	0.4	4.5	....	0.04	0.070
Feldspar, Peterhead .....	2.1	1.00	....	0.214	1.201

Four of these (including the mica of meta-sedimentary origin) were secondary minerals whose gas may have been produced entirely by chemical reactions in the tube, without having very great bearing upon the problem of the gas-content of primary minerals and rocks which have not undergone extensive weathering and alteration. The only rock tried, the gabbro, may be pointed out as unique in yielding only hydrogen without either of the oxides of carbon or nitrogen.

Armand Gautier,<sup>4</sup> in 1901, came to the conclusion that the gases which he obtained from several igneous rocks did not escape from inclusions, for the most part, but were products of chemical reactions at raised temperatures. A small quantity of gas was obtained by heating granite powder, moistened with pure water, up to 300° in a vacuum. By heating the same

<sup>1</sup> Mendeléef, *Prin. of Chem.*, transl. of Kamensky and Greenaway, vol. 1, pp. 364-365.

<sup>2</sup> H. Moissan, *Proc. Roy. Soc.*, vol. 60 (1896), pp. 156-160.

<sup>3</sup> M. W. Travers, *Proc. Roy. Soc.*, vol. 64 (1898), pp. 130-142.

<sup>4</sup> A. Gautier, *Comptes Rendus*, vol. 132, pp. 58-64, 189-194.

granite powder together with a mixture of two parts of sirupy phosphoric acid and one part of water to only 100°, he received more than 10 times as much gas as was evolved at 300° without the acid, or about 1.5 volumes.

Table 7 comprises Gautier's analyses of the gases expelled at red heat.

TABLE 7.

Rock.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Vol.
Granite, Vire I.....	Trace	14.80	4.93	2.24	77.30	0.83	} Av. 6.9
Granite, Vire II.....	1.71	8.98	5.12	1.09	82.80	0.42	
Granite, Vire III.....	0.69	14.42	5.50	1.99	76.80	0.40	
Granitoid porphyry, Esterel.....	0.00	59.25	4.20	2.53	31.09	2.10	7.6
Ophite, Villefranche I.....	3.44	28.10	3.91	1.40	63.28	0.05	} Av. 7.60
Ophite, Villefranche II.....	5.56	30.66	4.45	0.66	58.90	0.13	
Ophite, Villefranche III.....	0.45	35.71	4.85	1.99	56.29	0.68	
Lherzolite, Lherz.....	11.85	78.35	1.99	0.01	7.34	Trace	15.7

The rôle played by these gases in vulcanism, and their connection with thermal waters, is discussed in more recent papers.<sup>1</sup> Following Gautier, Hüttner<sup>2</sup> showed by a series of experiments that when a stream of dry carbon dioxide is passed over a rock powder at a temperature of 800°, carbon monoxide results, owing to a reduction of the dioxide, as this investigator believes, by some of the hydrogen given off from the rock. As the minerals orthite and gadolinite yielded no carbon monoxide, though abundant hydrogen, when gelatinized in hydrochloric acid, he came to the conclusion that this gas does not exist in rocks.

In 1905 there appeared a paper by Albert Brun,<sup>3</sup> "Quelques Recherches sur le Volcanisme," based upon studies of lavas from Vesuvius, Stromboli, and other Mediterranean volcanoes. While no complete gas analyses were undertaken, much experimentation was done, covering the expulsion of gases and vapors at or near the fusion point of the lavas. This author expresses the opinion that it is the liquefaction of the rock which produces the gases, these being engendered by chemical bodies contained within the lava itself. The gases recognized are nitrogen and its derivative ammonia, chlorine with derived hydrochloric acid, and hydrocarbons. The nitrogen is assigned to nitrides, and the ammonia to reactions between nitrides and hydrocarbons, while a dissociation of chlorides furnishes free chlorine which may take hydrogen from hydrocarbons to form hydrochloric acid. A source for hydrogen and carbon dioxide is recognized in hydrocarbon compounds, though Brun was less interested in the gases expelled below the melting-point of the lava.

<sup>1</sup> Gautier, *Comptes Rendus*, vol. 132, pp. 740-746 and 932-938; *Economic Geology*, vol. 1 (1906), pp. 688-697.

<sup>2</sup> K. Hüttner, *Zeitschrift für Anorg. Chem.*, 43 (1905), pp. 8-13.

<sup>3</sup> A. Brun, *Archives des Sciences phys. et naturelles*, Genève, 1905.

### METHOD OF PROCEDURE.

To obtain the gases for these investigations, the general methods of Graham, Mallet, and Wright were adopted, though the details of the apparatus were modified in many particulars. The gas is extracted from the rock material which has been finely pulverized, by heating the powder in a vacuum. For this purpose an apparatus consisting of a combustion-tube connected with a mercury-pump capable of producing and maintaining a vacuum of a fraction of a millimeter pressure is required. Simplicity being desirable in order to insure the uniform working of the pump in the presence of corrosive gases, such as hydrogen sulphide and sulphur dioxide, which attack and befoul the mercury, the most elementary type of Töpler<sup>1</sup> pump was used in these experiments.

To the receiving end of the pump a long, horizontal, calcium chloride drying-tube is fused. The ideal method would be to seal the combustion-tube containing the rock powder directly to the free end of this drying-tube. But inasmuch as the pump and drying-tube are both constructed of soft glass, whereas the tube in which the high-temperature combustions are to be made must, of necessity, consist of the most refractory glass, which can not be readily united to the fusible glass, one break in the system is unavoidable. This is made at the end of the drying-tube, which is ground so as to receive a tightly fitting hollow stopper of the same hard, blue Jena composition tubing as the combustion-tube. A 5-millimeter tube of blue Jena glass joins the combustion-tube to the stopper, and is taken of sufficient length to allow of repeated cutting and resealing to successive tubes, as they become useless from slow deformation under the combined influence of high temperature and vacuum.

The capillary exhaust-tube of the pump, dipping under mercury in a trough, is bent upward at its lower extremity, so as to deliver the gas expelled from the pump directly into the receptacle designed for holding it. For this purpose, a separatory funnel of about 125 cubic centimeters capacity, held by a clamp in an inverted position over the mercury trough, proved most serviceable.

In making an analysis, the rock specimen is first reduced to a powder of sufficient fineness to pass through a sieve of 30 meshes to the inch. A portion of this powder, roughly estimated to approach the maximum quantity which can with safety be placed in the combustion-tube, is then weighed and carefully poured into the tube through the hollow stopper, which, on account of its shape, serves as a funnel. Because the rock-dust in falling becomes somewhat packed, the tube must afterwards be held in a horizontal position, and gently shaken or tapped, to establish a free passageway for the gases, extending the entire length of the tube; otherwise, upon attempting to exhaust, preparatory to heating, the air entrapped in the powder, having no avenue of ready escape, will expand so rapidly as to force some of the material into the drying-tube.

Thus carefully filled, the tube is placed in the combustion-furnace, which stands upon a table of height such that the stopper end of the com-

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<sup>1</sup> Described by Travers, *A study of gases*, pp. 5-10.



bustion-tube meets approximately the ground end of the calcium chloride tube coming from the pump. The pump itself, installed upon a specially constructed table resting on jacks, can be raised or lowered, or tilted at a slight angle in any direction necessary to enable the stopper protruding from the furnace to fit exactly into the drying-tube. As the whole apparatus is now rigid glass from end to end, care is required in fitting the two parts together, lest there be strain sufficient to cause serious fracture. To prevent leakage during the extraction of the gas, the ground-glass connection (the only source of leakage) is completely incased in a thick coating of paraffine.<sup>1</sup>

The air in the apparatus is now pumped off until the exhaustion can be carried no further, at which point the pressure may be in the neighborhood of 0.01 millimeter. If allowed to stand for several days this vacuum remains entirely without change. When ready, the burners in the furnace are lighted, the separating funnel in which the gases are to be collected is filled with mercury, and the evolution of the gas is under way. As fast as the gases are liberated by the heat they are pumped over into the collecting-funnel—a process usually requiring about 3 or 4 hours before the last traces of gas have been expelled.

#### ANALYSIS OF THE GAS.

After constant temperature has been established in the room, the gas is drawn from the receiver into a Lunge nitrometer and the carbon dioxide and hydrogen sulphide absorbed by the introduction of a cubic centimeter of 30 per cent potassium hydroxide solution. The remaining gas is transferred to a gas-burette, filled with water, after which the remainder of the analysis is carried on according to the method described by Hempel.<sup>2</sup> From the potassium hydroxide solution the amount of hydrogen sulphide absorbed is determined by titration with N/100 iodine solution. If it be desired to measure the quantity of helium and argon, the gas remaining after the removal of all the constituents, except nitrogen and these inert gases, is passed over metallic calcium heated to redness.<sup>3</sup> This absorbs the nitrogen, leaving only helium and argon, which are examined spectroscopically.

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<sup>1</sup> Whenever rocks containing a large proportion of quartz are tested, it is necessary to substitute a porcelain tube, since quartz scratches glass, causing it to crack when heated. The connections are readily made tight with paraffine.

<sup>2</sup> Hempel, *Methods of gas analysis*: Technical method.

<sup>3</sup> Travers, *A study of gases*, p. 102.

## THE ANALYSES.

The analyses are numbered in table 8 in the order in which they were made, and therefore furnish a chronological account of these investigations. At the commencement of these studies, it being deemed advisable to make a rapid survey of the field and establish the range of the phenomenon, in order to direct later experiments more intelligently, less attention was given to securing the most trustworthy method of extracting the gas. Twenty-two analyses were made during the preliminary trial stage, before the apparatus was overhauled and sealed glass connections substituted for rubber tubing. As it was difficult to prevent a slight leakage of air into the tubes of the original apparatus, the first 22 analyses are characterized by a higher percentage of nitrogen than those made afterwards under more favorable conditions. Hydrogen sulphide was not determined in the first 17 analyses.

Table 8 gives the percentage of each gas in the total volume of gas; and the volume of each gas (at 0° and 760 mm. pressure) per unit-volume of rock.

TABLE 8.

Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH <sub>4</sub> ).	Hydrogen (H <sub>2</sub> ).	Nitrogen (N <sub>2</sub> ).	Total.
1. Medium-grained white granite, rather low in quartz.	P. et. Vol.	.... ....	19.20 .28	4.94 .07	4.85 .07	64.01 .92	7.00 .10	100 1.44
2. Very coarse granite with prominent pink feldspar phenocrysts.	P. et. Vol.	.... ....	11.56 .42	2.41 .09	2.70 .10	80.29 2.94	3.04 .11	100 3.66
3. Keewatin schist from Mesabi district, Minn. From oldest known series of Lake Superior region, highly carbonated. (Specimen 40896, Slide 15466, U. S. G. S.) From C. R. Van Hise.	P. et. Vol.	.... ....	63.76 7.67	2.33 .28	.43 .05	31.66 3.82	1.82 .22	100 12.04
4. Laurentian dike rock from Lake Superior. (Specimen 41879, Slide 16673, U. S. G. S.) Gneiss from contact of Keewatin greenstone and Laurentian granite near Rat Portage, Ont. From C. R. Van Hise.	P. et. Vol.	.... ....	14.74 .31	3.93 .08	2.85 .06	71.88 1.50	6.60 .13	100 2.08
5. Kinderhook shale. Burlington, Iowa. From Stuart Weller.	P. et. Vol.	.... ....	91.65 9.28	3.46 .35	1.24 .12	2.18 .22	1.47 .15	100 10.12
6. Portage shale, Ithaca, N. Y. From Dr. Weller. (Nitrogen omitted from analysis because of leakage of air into tube.)	P. et. Vol.	.... ....	39.80 1.47	22.65 .83	4.25 .16	33.30 1.23	.... ....	100 3.69
7. Muscovite, Canada; material taken from a large slab of mica in Walker Museum collection.	P. et. Vol.	.... ....	70.33 1.26	6.59 .12	2.71 .04	5.49 .10	14.85 .27	100 1.79
8. Potsdam sandstone, Baraboo, Wis. Treated with HCl to remove any carbonate from the surface of the grains.	P. et. Vol.	.... ....	45.70 .47	17.19 .18	.78 .01		36.32 .38	100 1.04
9. Pike's Peak granite, from carriage-road across divide between N. Cheyenne and Bear Creek canyons. A coarse-grained, yellowish-pink granite constituting the great mass into which the finer-grained pinkish granite of the peak proper has been intruded.	P. et. Vol.	.... ....	60.74 .37	9.24 .05	2.70 .02	6.47 .04	20.85 .12	100 .60
10. Rhyolite, Marble Mountain on north slopes of San Francisco Peaks, Ariz.	P. et. Vol.	.... ....	44.15 .22	16.40 .08	7.14 .04	5.81 .03	26.50 .13	100 .50
11. Keweenaw diabase, from 1 mile east of Dresser Junction, Polk Co., Wis. (a lava flow).	P. et. Vol.	.... ....	12.05 .59	.93 .05	3.83 .19	78.14 3.83	5.05 .25	100 4.91
12. Quartzite schist, collected 2 miles southwest of Baraboo, Wis.	P. et. Vol.	.... ....	46.05 .16	20.68 .07	7.93 .03	7.29 .03	18.05 .06	100 .35
13. Andesite. Silver Creek Basin, Ouray Co., Colo.	P. et. Vol.	.... ....	(1) ....	36.28 .09	7.61 .02	27.91 .08	28.20 .08	100 .27
14. Coarse porphyry from dump pile of San Pedro Mine, Ouray Co., Colo.	P. et. Vol.	.... ....	(1) ....	16.15 .05	7.51 .02	73.00 .22	3.34 .01	100 .30

<sup>1</sup> Carbonated.

TABLE 8—Continued.

Specimen No. and remarks.	P. ct. or vol.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
15. Gabbro diorite from about 13,000 ft. elevation on south side of Mt. Sneffels, Colo.	P. ct. ....	....	22.01	5.54	2.05	62.33	8.07	100
16. Coarse-grained gabbro diorite, summit of Mt. Sneffels, Colo.	Vol. ....	....	.40	.10	.04	1.13	.14	1.81
	P. ct. ....	....	( <sup>1</sup> )	10.08	1.92	79.15	8.85	100
	Vol. ....	....	.12	.02	.97	.11	.12	1.22
<sup>2</sup> 17. Coarse orthoclase gabbro, from bluff about 100 paces east of the "Pavilion," in N. $\frac{1}{2}$ sec. 28, Duluth, Minn. Specimen 4602, Slide 1602, U. S. G. S. This belongs to the St. Louis River series (6000 ft. thick) which is the lowest member of the Keeweenaw at Duluth. Collection of R. D. Irving. References: Monograph V, U. S. G. S., pp. 50-53, 266, and 268-275.	P. ct. ....	....	12.08	3.20	1.79	73.95	8.97	100
	Vol. ....	....	.44	.12	.07	2.68	.32	3.63
18. Hamilton shale, along the Susquehanna, 1 mile south of Marysville, Pa.; a very hard indurated shale.	P. ct. 0.04	16.52	6.91	2.90	57.89	15.75	100	
	Vol. .00	.41	.17	.07	1.15	.40	2.50	
<sup>3</sup> 19. Massive granite porphyry, Horse Race, near Upper Quinnesec Falls, Menominee district. Specimen 11082, Slide 5700, U. S. G. S. Collection G. H. Williams.	P. ct. ....	51.26	10.55	.86	34.19	3.14	100	
	Vol. ....	3.51	.72	.06	2.34	.22	6.85	
420. Fine-grained gneiss, same rock-mass as No. 19. Specimen 11085, Slide 5702, U. S. G. S. Collection G. H. Williams.	P. ct. .24	67.24	8.31	.79	14.96	8.46	100	
	Vol. .00	1.89	.23	.02	.43	.23	2.80	
421. Fine-grained banded gneiss, same rock-mass as Nos. 19 and 20. Specimen 11084, Slide 5701, U. S. G. S. Collection G. H. Williams.	P. ct. ....	71.47	12.20	.68	14.75	.90	100	
	Vol. ....	6.63	1.13	.06	1.37	.08	9.27	
22. Laurentian granite, Marquette district, Mich. Specimen 14392, Slide 9259. From C. R. Van Hise.	P. ct. ....	64.41	4.41	.93	25.15	5.10	100	
	Vol. ....	1.89	.13	.03	.74	.15	2.94	
23. Schist with chloritoid, Black Hills, S. Dak. Specimen 14928, Slides 7671, 14968, and 14969. References, Bull. 239, pl. xiv. Described by Van Hise, Bull. G. S. A., vol. 1. Developed by anamorphism of graywacke-slate series through the influence of batholithic granite.	P. ct. ....	12.49	2.56	1.10	82.58	1.32	100	
	Vol. ....	.46	.10	.04	3.07	.05	3.72	
24. Pink orthoclase granite, North Carolina. Obtained from Blake & Co., marble cutters, Chicago.	P. ct. .13	23.86	8.28	3.83	57.31	6.59	100	
	Vol. .00	.16	.05	.02	.38	.04	.65	
25. Dark olive-gray granite, Quincy, Mass. From Blake & Co.	P. ct. .10	24.56	5.48	3.40	64.84	1.62	100	
	Vol. .00	.39	.09	.06	1.04	.02	1.60	
<sup>5</sup> 26. Fine-grained gray granite, Russia. From Blake & Co.	P. ct. .03	60.43	6.15	33.36			100	
	Vol. .00	1.79	.18	.99			2.96	
27. Baltimore gneiss, Williams' quarry, Roberts Road, 2 miles west of Bryn Mawr, Pa. From F. Bascom.	P. ct. .01	2.95	2.05	2.99	91.11	.89	100	
	Vol. .00	.13	.10	.14	4.32	.04	4.73	
28. Baltimore gneiss, Schuylkill River section, 1 mile SE. of Spring Mill, Pa. From F. Bascom.	P. ct. 4.91	22.17	3.69	1.74	65.85	1.64	100	
	Vol. .30	1.35	.22	.11	4.02	.10	6.10	
29. Wissahickon mica gneiss, Fovelton's quarry, on Childs estate, 2 miles SW. of Bryn Mawr, Pa. From F. Bascom.	P. ct. .53	19.07	6.67	2.21	67.33	4.19	100	
	Vol. .00	.19	.07	.02	.65	.04	.97	
30. Wissahickon mica gneiss, Rose Glen quarry, W. bank of Schuylkill River. A more solid, compact rock than No. 29, which was sericitic. From Dr. Bascom.	P. ct. .06	8.26	3.35	3.50	81.65	3.18	100	
	Vol. .00	.19	.08	.08	1.90	.08	2.33	
31. Cambrian gneiss, West Grove Ridge, Coatesville Quadrangle, Pa. From Dr. F. Bascom. Resembles an impure sandstone whose argillaceous material had been altered to mica during the metamorphic process; crushes to a sandy powder like a sandstone.	P. ct. ....	33.99	11.43	1.21	49.02	4.36	100	
	Vol. ....	.26	.09	.01	.37	.03	.76	

<sup>1</sup> Carbonated.<sup>2</sup> No. 17. Analysis (by Strong): SiO<sub>2</sub>, 49.15; Al<sub>2</sub>O<sub>3</sub>, 21.90; Fe<sub>2</sub>O<sub>3</sub>, 6.60; FeO, 4.54; CaO, 8.22; MgO, 3.03; Na<sub>2</sub>O, 3.83; K<sub>2</sub>O, 1.61; H<sub>2</sub>O, 1.92; 100.80.<sup>3</sup> No. 19. Analysis (Riggs, Bull. 62, p. 113): SiO<sub>2</sub>, 54.83; Al<sub>2</sub>O<sub>3</sub>, 25.49; Fe<sub>2</sub>O<sub>3</sub>, 1.61; FeO, 1.65; CaO, 6.08; MgO, 1.96; Na<sub>2</sub>O, 5.69; K<sub>2</sub>O, 1.87; H<sub>2</sub>O, 1.18; CO<sub>2</sub>, .18; 100.54.<sup>4</sup> Nos. 19, 20, and 21 were collected from an intrusion of granite-gneiss into greenstone, which has been called Upper Huronian by Brooks, the granite-gneiss being placed at the top of the Upper Huronian. Bulletin 62, p. 26. This series shows a gradation from massive porphyritic granite to very fine-banded gneiss. No. 19 is from the center of the intrusive dike, and grades almost imperceptibly on both sides into the fine-grained gneiss of which No. 20 is the type. No. 21 is similar to No. 20, being on the sides, but is banded. This rock is more basic than typical granite, being more like a diorite in composition. The low gas-volume of No. 20 in comparison with the two other specimens is perhaps to be explained by the fact that it is a much more porous rock, crumbling readily to a fine powder on the anvil.<sup>5</sup> Owing to an accident during the explosion it was impossible to determine the relative amounts of CH<sub>4</sub>, H<sub>2</sub>, and N<sub>2</sub>, but the violence of the explosion suggests that there was little N<sub>2</sub> present.

TABLE 8—Continued.

Specimen No. and remarks.	P. ct. or vol.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
132. Olivine free, saussuritized schistose gabbro, Menominee district, Lake Superior region. Specimen 11166, Slide 5747. Described by Williams, Bull. 62, pp. 62-76. An extremely altered gabbro, containing calcite, sericite, chlorite, and leucocene.	P. ct. Vol.	0.07 .02	67.50 20.07	1.95 .58	0.69 .20	28.71 8.54	1.08 .32	100 29.73
33. Laurentian gneiss, Marquette district, Mich. Specimen 14718, Slide 9361, U. S. G. S. From C. R. Van Hise.	P. ct. Vol.	.07 .00	28.81 .85	5.07 .15	2.64 .07	59.66 1.79	4.25 .12	100 2.98
34. Keewatin greenstone, Mesabi district. Oldest known series of the Lake Superior region. Specimen 40785, Slide 15420, U. S. G. S. Considerable water was given off when powder was heated. From C. R. Van Hise.	P. ct. Vol.	.58 .19	62.38 20.08	3.60 1.16	.28 .09	31.38 10.10	1.78 .57	100 32.19
35. Keweenaw diabase, railroad cut south of schoolhouse in Taylor's Falls, Minn.	P. ct. Vol.	.45 .01	7.05 .25	1.57 .06	1.77 .06	87.66 3.15	1.50 .06	100 3.59
36. Olivine gabbro, from foot of cliff at N.E. headland of Beaver Bay, near Duluth, Minn. Specimen 4601, Slide 4601, U.S.G. S. Collection R. D. Irving. (References: Mon. v. U. S. G. S., Lithol., pp. 37-45. Location on map, p. 305; description, p. 309.)	P. ct. Vol.	.46 .00	19.97 .16	7.91 .07	3.96 .04	62.54 .52	5.16 .05	100 .84
37. Oglethorpe blue granite, near Elberton, Elbert Co., Ga. From S. W. McCallie.	P. ct. Vol.	.07 .00	47.06 1.13	4.74 .11	1.57 .03	44.33 1.06	2.23 .05	100 2.38
38. Stone Mountain granite, Stone Mountain, De Kalb Co., Ga. From S. W. McCallie.	P. ct. Vol.	.10 .00	10.93 .08	4.85 .03	1.55 .01	77.20 .60	5.37 .04	100 .76
39. Coarse reddish Archean granite, Big Stone Lake, near Ortonville, Minn. From Blake & Co. Microcline and orthoclase form large crystals; quartz is abundant, but biotite is rather sparse. Described in Geol. of Minn., vol. 5, p. 814.	P. ct. Vol.	.11 .00	87.84 1.20	3.51 .05	1.10 .01	3.61 .05	3.83 .05	100 1.36
40. Ortonville granite, biotite crystals of last specimen separated from quartz and feldspar by mercuric iodide specific gravity solution.	P. ct. Vol.	1.61 .22	92.40 12.45	1.71 .23	.45 .06	2.23 .30	1.60 .21	100 13.47

Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Hydrocarbon vapors.	Sulphur dioxide (SO <sub>2</sub> ).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Heavy hydrocarbons.	Methane (CH <sub>4</sub> ).	Hydrogen (H <sub>2</sub> ).	Nitrogen (N <sub>2</sub> ).	Total.
41. Hamilton shale, Newsom's Station, 15 miles W. of Nashville, Tenn. From Miss Augusta T. Hasslock. An exceedingly bituminous shale emitting a strong odor resembling that of asphalt when struck with a hammer. What part of this gas really existed within the rock in the gaseous state can not be stated; most of it probably came from decomposition of organic matter present. Heavy brown tars also produced. No determination of hydrocarbon vapors was made.	P. ct. Vol.	30.94 29.38	.... ....	.... ....	21.17 20.10	4.61 4.38	4.29 4.07	38.99 37.03	.... ....	.... ....	100 94.96
242. Oil-rock from lead-zinc mine near Platteville, Wis. From H. F. Bain.	P. ct. Vol.	6.79 3.90	11.11 6.38	.... ....	18.12 10.43	8.40 4.82	4.00 2.30	35.98 20.67	13.18 7.57	2.16 1.24	100 57.46
243. Sillimanite gneiss, St. Jean de Matha, Quebec. From F. D. Adams.	P. ct. Vol.	.... ....	.... ....	54.74 2.76	40.55 2.05	1.64 .09	.... ....	.61 .03	1.10 .05	1.36 .07	100 5.05

<sup>1</sup> No. 32. Analysis: SiO<sub>2</sub>, 38.05; Al<sub>2</sub>O<sub>3</sub>, 24.73; FeO, 5.65; Fe<sub>2</sub>O<sub>3</sub>, 6.08; CaO, 1.25; MgO, 11.58; Na<sub>2</sub>O, 2.54; K<sub>2</sub>O, 1.94; H<sub>2</sub>O, 7.53; CO<sub>2</sub>, 0.93; 100.28. (R. B. Riggs, Bull. 62, p. 76.)

<sup>2</sup> Probably only a small part of gas was really present in the gaseous condition, the analysis being made to show what a bituminous shale may yield.

<sup>3</sup> A metamorphosed slate of the Grenville series. Reference: Am. Jour. Sci., vol. 50, p. 58. Described as a fine-grained garnetiferous sillimanite gneiss containing much quartz and orthoclase. Graphite and pyrite also present, causing the gneiss to weather to a very rusty color. Analysis by N. N. Evans, of McGill University: No. 43. SiO<sub>2</sub>, 61.96; TiO<sub>2</sub>, 1.66; Al<sub>2</sub>O<sub>3</sub>, 19.73; Fe<sub>2</sub>O<sub>3</sub> and FeO, 4.60; FeS<sub>2</sub>, 4.33; MnO, trace; CaO, 0.85; MgO, 1.81; Na<sub>2</sub>O, 0.79; K<sub>2</sub>O, 2.50; H<sub>2</sub>O (ignition), 1.82; 99.55.



TABLE 8—Continued.

Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH <sub>4</sub> ).	Hydrogen (H <sub>2</sub> ).	Nitrogen (N <sub>2</sub> ).	Total.
44. Nephelite syenite, north of Mountain Lake, Tp. of Methuen, Ontario. F. D. Adams. Of igneous origin.	P. ct. .... Vol. ....	.... .29	42.42 .29	8.76 .05	5.49 .04	36.33 .25	7.00 .05	100 .63
45. Iron-bearing basalt, Ovivak, Disco Island, Greenland.	P. ct. .... Vol. ....	0.03 .00	46.50 3.74	21.63 1.74	2.09 .17	27.88 2.24	1.87 .16	100 8.05
46. Magnetite sand, Snake River bed, Idaho, from Oskar Eckstein. Separated from impurities by magnet.	P. ct. .... Vol. ....	.... .22	83.91 2.22	10.19 .27	5.90 .16			100 2.65
47. Andesite, Red Mountain, NW. of San Francisco Peaks, Ariz. Collected by W. W. Atwood. Mr. Arthur Taylor describes this rock as an andesite porphyry whose ground-mass (96 p. ct. of the whole) consists of 48 p. ct. pyroxene, 31 p. ct. plagioclase (labradorite), and 12 p. ct. magnetite. The phenocrysts are lime-soda feldspar, augite, hornblende, and magnetite. Occurs as irregular blocks cemented in the tuff or volcanic breccia of which Red Mountain is built.	P. ct. .... Vol. ....	.01 .00	80.38 5.12	9.02 .57	4.74 .30	1.84 .12	4.03 .26	100 6.37
48. Pyroxene crystals, Red Mountain, Ariz. Collected by W. W. Atwood. These crystals, ranging in size from a bean to a small marble, were found loose on the surface, having weathered out of the breccia.	P. ct. .... Vol. ....	8.90 .10	62.62 .69	14.46 .16	1.30 .01	7.01 .08	5.71 .06	100 1.10
49. Rhyolite vitrophyre, ridge N. of Park Basin, Telluride Quadrangle, Colo. Specimen No. 3054 U. S. G. S. A lava flow belonging to the intermediate series. From Whitman Cross.	P. ct. .... Vol. ....	.... .23	92.66 2.33	1.94 .05	1.39 .03	2.71 .07	1.30 .03	100 2.51
50. Nephelite melilite basalt, Uvalde Quadrangle, Tex. Collected by T. W. Vaughan. Described (Uvalde Folio, p. 4) as a very fine-grained, dark-colored rock, with the nephelite invisible to the naked eye. Contains little or no feldspar and comparatively little nepheline. Olivine and augite are the most important constituents. The presence of melilite indicates unusual amount of lime in magma. Age doubtfully placed as Eocene.	P. ct. .... Vol. ....	1.99 .05	40.32 1.07	7.55 .20	2.18 .06	44.18 1.16	3.78 .10	100 2.64
51. Shonkinite, Highwood Mountains, Mont. Core rock of Shonkin stock. Described (Ft. Benton Folio, p. 3) as a rock of the syenite family very rich in augite, containing accessory olivine and black mica. While the chief light-colored constituent is orthoclase, nephelite and sodalite are present in varying amounts. An intrusive of probably Eocene age. Collected by W. H. Weed.	P. ct. .... Vol. ....	.04 .00	8.85 .11	4.97 .06	3.94 .05	78.08 .95	4.12 .05	100 1.22
52. Theralite, from the laccolites on Upper Shield River Basin, Crazy Mountains, Mont. U. S. National Museum No. 73138. Collected by W. H. Weed. Described (Little Belt Mountains Folio, p. 4) as a dark-gray basaltic rock commonly occurring in sheets, but rarely in dikes. Porphyritic crystals of augite form the most prominent phenocrysts, though large plates of brown mica are common. Colorless part of the ground-mass is a granular mixture of nephelite and lime-soda feldspars. Eocene age.	P. ct. .... Vol. ....	.01 .00	48.18 1.08	7.63 .17	1.58 .04	41.21 .93	1.39 .03	100 2.25
53. Quartz syenite porphyry, summit of Engineer Mountain, Silverton Quadrangle, Colo. No. 3728 U. S. G. S. From Dr. Cross. Described (Silverton Folio, p. 11) as strongly porphyritic, with many glassy orthoclase crystals colored reddish by fine	P. ct. .... Vol. ....	.... ....	(1) .....	24.89 .11	17.22 .08	50.22 .22	7.53 .03	100 .41

<sup>1</sup> Carbonated.

TABLE 8—Continued.

Specimen No. and remarks.	P. ct. or vol.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
ferritic pigment. Also phenocrysts of quartz, plagioclase, biotite, and hornblende; dark, ash-gray ground-mass. Either an intrusive or resting upon andesitic tuffs of Silverton series.								
54. Altered Jurassic shale, LaPlata Quadrangle, Colo. Contact zone below Indian Trail Ridge. Alteration due to intrusion of vogesite. (See analysis No. 84.) From Dr. Cross.	P. ct. Vol.	0.16 .00	(1) .....	22.09 .15	5.41 .04	65.96 .45	6.38 .04	100 .68
55. Garnetiferous gneiss, Darwin's Falls, Tp. of Rawdon, Quebec. Probably of sedimentary origin. From F. D. Adams.	P. ct. Vol.	13.27 .11	20.26 .16	9.51 .07	2.11 .02	52.20 .41	2.65 .02	100 .79
56. Hornblende syenite, Cape Elizabeth, Me. From the drift. U. S. N. M. No. 39035.	P. ct. Vol.	.03 .00	6.13 .16	2.76 .07	1.03 .03	88.77 2.22	1.28 .03	100 2.50
57. Granite porphyry boulder, northern New York.	P. ct. Vol.	3.35 .04	(1) .....	22.19 .27	1.75 .02	69.37 .85	3.34 .04	100 1.22
58. Intrusive in Highwood Mountains, E. side of divide, Highwood Gap, Ft. Benton Quadrangle, Mont. Microscopically resembles a diorite; probably of Eocene age. Collected by W. H. Weed.	P. ct. Vol.	..... .....	31.91 .28	8.44 .07	4.44 .04	51.25 .45	3.96 .03	100 .87
<sup>2</sup> 59. Nevadite, Chalk Mountains, Ten-mile district, Colo. From U. S. Nat. Mus. Described in Monograph XII, p. 345. Contains numerous dark quartz crystals and clear sanidines, embedded in a light gray ground-mass made up of sanidine, plagioclase, and quartz, but containing little biotite or magnetite.	P. ct. Vol.	..... .....	57.19 .15	19.29 .06	4.70 .01	7.53 .02	11.28 .03	100 .27

Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Sulphur dioxide (SO <sub>2</sub> ).	Heavy hydrocarbons.	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH <sub>4</sub> ).	Hydrogen (H <sub>2</sub> ).	Nitrogen (N <sub>2</sub> ).	Total.
60. Diorite plug in Cretaceous shales, between forks of Deep Creek on ridge from Mt. Ruffner, 3 miles from lower contact, Telluride Quadrangle, Colo. No. 2872 U. S. G. S. From Whitman Cross.	P. ct. Vol.	2.06 .03	..... .....	0.16 .00	14.55 .22	4.18 .06	3.41 .05	71.37 1.10	4.27 .06	100 1.52
61. Diabase, Nahant, Mass.....	P. ct. Vol.	2.18 .19	..... .....	..... .....	56.53 4.91	2.36 .21	1.36 .12	35.93 3.13	1.64 .15	100 8.71
62. Andesite, Rosita Hills, Custer Co., Colo., from summit of small hill east of spring on Rosita Road. Dike facies of Pringle type. (See report on Geology of Silver Cliff, Rosita Hills area, by Whitman Cross.)	P. ct. Vol.	.06 .00	..... .....	..... .....	(1) .....	35.67 .27	6.67 .05	40.02 .30	17.58 .13	100 .75
63. Anorthosite, sheared igneous rock, 2.5 miles from Chertsey, Quebec. F. D. Adams.	P. ct. Vol.	.02 .00	..... .....	..... .....	71.99 2.36	8.40 .27	.54 .02	17.17 .56	1.88 .06	100 3.27
64. Andesite, Lipari Islands.....	P. ct. Vol.	.06 .00	..... .....	..... .....	70.29 .56	4.85 .04	.98 .01	21.62 .17	2.20 .02	100 .80
65. Fine-grained gneiss, lot 5, Concession I, Harburn Tp., Ontario. Dr. Adams regards this as almost certainly an altered sediment, for it occurs in beds interstratified with limestone. Impregnated with pyrite and contains graphite. Analysis shows it to be a tephomose.	P. ct. Vol.	..... .....	85.12 4.15	..... .....	13.89 .68	0.99 .05				100 4.88
66. Gneiss of igneous origin, lot 28, R. 9, Wollaston Tp., Ontario. F. D. Adams.	P. ct. Vol.	.04 .00	..... .....	..... .....	19.35 .28	8.91 .13	2.20 .03	64.24 .95	5.26 .08	100 1.47
67. Feather amphibolite, lot 16, R. 12, Wollaston Tp., Ontario. Probably of sedimentary origin. F. D. Adams.	P. ct. Vol.	.22 .00	..... .....	..... .....	(1) .....	54.45 .49	2.89 .03	35.62 .32	6.82 .06	100 .90

<sup>1</sup> Carbonated.<sup>2</sup>No. 59. Analysis (p. 589): SiO<sub>2</sub>, 74.45; Al<sub>2</sub>O<sub>3</sub>, 14.72; FeO, 0.56; MnO, 0.28; CaO, 0.38; MgO, 0.37; K<sub>2</sub>O, 4.53; Na<sub>2</sub>O, 3.97; H<sub>2</sub>O, 0.66; P<sub>2</sub>O<sub>5</sub>, 0.01; 100.38.

TABLE 8—Continued.

Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH <sub>4</sub> ).	Hydrogen (H <sub>2</sub> ).	Nitrogen (N <sub>2</sub> ).	Oxygen (O <sub>2</sub> ).	Total.
68. Amphibolite, Maxwell's Crossing, Glamorgan Tp., Ontario. A highly altered limestone. Dr. Adams.	P. ct. Vol.	0.06 .00	( <sup>1</sup> ) ....	10.94 .26	2.11 .05	84.01 2.01	2.88 .06	.... ....	100 2.38
69. Rice rock, Canadian Pacific R. R. 0.25 mile east of Sudbury, Ontario. Probably an altered sediment of Huronian age. Dr. Adams.	P. ct. Vol.	4.86 .16	14.67 .47	5.14 .16	1.45 .05	71.89 2.32	1.99 .06	.... ....	100 3.22
70. Andesite, Granite Mountain, Iron Co., Utah. Alaccolite in Palaeozoic sediments. C. K. Leith.	P. ct. Vol.	.03 .00	77.50 2.66	4.75 .16	.95 .03	15.35 .53	1.42 .05	.... ....	100 3.43
71. Vein quartz, Granite Mountain, Iron Co., Utah. Associated with iron ore which has developed along the contact of the laccolite and intruded limestone. According to Leith it was presumably derived from the andesite (No. 70).	P. ct. Vol.	.... ....	13.93 .11	11.26 .09	4.00 .03	64.40 .53	6.41 .05	.... ....	100 .81
72. Phonolite trachyte, east part of Bull Mountain, Pike's Peak Quadrangle, Colo. No. 2488 U. S. G. S. Described by Cross (Pike's Peak Folio, p. 3) as a dense, grayish-green rock with tabular crystals of sanidine, which give it a typical porphyritic texture.	P. ct. Vol.	.27 .00	69.37 .76	4.85 .05	2.67 .03	17.16 .19	5.69 .06	.... ....	100 1.08
73. Coarse diorite boulder from Bluehill sheet, Penobscot Bay Quadrangle, Me. From E. S. Bastin.	P. ct. Vol.	3.28 .06	14.99 .27	3.78 .07	2.00 .04	72.83 1.29	3.12 .05	.... ....	100 1.78
74. Diorite, Deer Isle sheet, Penobscot Bay Quadrangle, Me. No. 1157. From E. S. Bastin.	P. ct. Vol.	1.44 .07	4.65 .21	.78 .04	4.38 .20	85.62 3.95	3.13 .14	.... ....	100 4.61
75. Potsdam sandstone, upper narrows of the Paraboo, Ablemans, Wis. Hard, indurated white sandstone, not far from the contact with the quartzite.	P. ct. Vol.	.15 .00	27.29 .09	15.12 .05	5.88 .02	37.86 .13	13.70 .05	.... ....	100 .34
76. Potsdam sandstone, Ablemans, Wis. ....	P. ct. Vol.	.08 ....	9.67 .05	15.42 .07	3.70 .02	52.11 .23	19.02 .08	.... ....	100 .45
77. Huronian quartzite, South Range, near Paraboo, Wis.	P. ct. Vol.	.13 .00	25.12 .11	9.53 .04	2.71 .01	55.43 .24	7.08 .03	.... ....	100 .43
78. Permian red sandstone, Garden of the Gods, near Colorado City, Colo.	P. ct. Vol.	.05 .00	( <sup>1</sup> ) ....	60.69 .71	6.27 .07	27.28 .32	5.71 .06	.... ....	100 1.16
79. Topaz quartz-porphyr, Schneckenstein, near Auerbach, Saxony.	P. ct. Vol.	trace .00	33.41 .32	8.16 .08	4.87 .05	45.40 .44	8.15 .03	.... ....	100 .97
80. St. Peter sandstone, Minnehaha Creek, below the falls, Minneapolis, Minn. A soft, remarkably white, coarse-grained sandstone. Before heating in the tube the grains were washed with dilute HCl.	P. ct. Vol.	2.6 .00	56.5 .02	9.6 .00	15.7 .01	1.7 .00	13.9 .01	.... ....	100 .04
81. St. Peter sandstone, Minnehaha. The sand No. 80, pulverized and heated a second time.	P. ct. Vol.	.... ....	6.40 .03	13.73 .07	2.41 .01	35.19 .17	42.27 .21	.... ....	100 .49
82. Quartzite belonging to Grenville Series, Darwin's Falls, Rawdon Tp., Quebec. From F. D. Adams.	P. ct. Vol.	37.65 .23	35.05 .21	7.12 .04	2.31 .01	15.60 .09	2.27 .01	.... ....	100 .59
83. Quartz crystals, Lincoln Co., N. C. Beautiful crystals whose perfectly formed faces indicated that they were formed from aqueous solution. Entirely transparent and without visible inclusions.	P. ct. Vol.	1.7 .00	30.0 .03	7.2 .00	6.4 .00	14.4 .01	35.1 .03	5.2 .00	100 .08
384. Vogesite, Indian Trail Ridge, La Plata Quadrangle, Colo. (a sheet in the Gunnison shales). A fine-grained greenish rock containing about equal amount of feldspars and feric minerals, and more augite than hornblende; feldspars much sericitized and obscured by chlorite, epidote, and calcite. Described in La Plata Folio, p. 7. From Dr. Cross. Allied type analyzed by W. F. Hillebrand.	P. ct. Vol.	Undet ....	( <sup>1</sup> ) ....	10.58 .14	2.48 .03	82.53 1.08	4.41 .05	.... ....	100 1.30

<sup>1</sup> Carbonated.

<sup>2</sup> The identical sand used in No. 75, powdered, and heated a second time. This experiment was to determine whether gas which was unable to escape might not still remain within the sand grains. As this powder yielded more gas than the fresh sand, most of the gas in the first trial apparently came from the surface or near the surface of the grains.

<sup>3</sup> No. 84. Analysis: SiO<sub>2</sub>, 43.98; Al<sub>2</sub>O<sub>3</sub>, 13.30; Fe<sub>2</sub>O<sub>3</sub>, 3.67; FeO, 6.92; MgO, 7.03; CaO, 10.66; Na<sub>2</sub>O, 2.15; K<sub>2</sub>O, 1.64; H<sub>2</sub>O, 1.94; TiO<sub>2</sub>, 1.18; CO<sub>2</sub>, 6.46; P<sub>2</sub>O<sub>5</sub>, .32; FeS<sub>2</sub>, .54; etc. .36; 100.15.

TABLE 8—Continued.

Specimen No. and remarks.	P. ct. or vol.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	O <sub>2</sub> .	Total.
85. Keweenawan diabase; drill core from Franklin Junior Hole No. 3, near Houghton, Mich. From A. C. Lane. This piece came from a depth of 524 feet, measured along a line 48° from the horizontal. Overlaying drift amounts to 110 feet, so that the preglacial covering of specimen was in the neighborhood of 315 feet, plus thickness of rock removed by glaciers. This specimen is from a massive flow of opfite, 62 feet in thickness.	P. ct. Vol.	.03 .00	33.61 1.31	2.40 .09	2.35 .09	60.24 2.34	1.37 .05	.... ....	100 3.88
186. Diabase, Nahant, Mass. Material from same specimen as No. 61.	P. ct. Vol.	.04 .00	61.25 8.51	2.47 .34	1.32 .18	33.69 4.68	1.23 .17	.... ....	100 13.88
287. Diabase, Nahant, Mass. Material from same specimen as No. 86.	P. ct. Vol.	.... ....	25.23 .06	20.15 .05	6.36 .01	21.21 .05	27.05 .06	.... ....	100 .23
388. Diabase, Nahant, Mass. Material from same specimen as Nos. 86 and 87.	P. ct. Vol.	13.30 .21	38.19 .62	9.01 .14	3.95 .06	38.80 .54	1.75 .03	.... ....	100 1.60
89. Albite crystals, Hebron, Maine.....	P. ct. Vol.	.... ....	17.09 ....	14.06 ....	6.80 ....	49.95 ....	12.10 ....	.... ....	100 ....
90. Wollastonite, Harrisville, Lewis Co., N. Y. Taken from a large specimen of pure white wollastonite and reduced to a powder in an agate mortar. No suggestion of any iron. Acid liberated very little carbon dioxide from powder. Walker Museum Collection.	P. ct. Vol.	.... ....	87.13 2.37	6.77 .18	.85 .02	2.16 .06	3.09 .08	.... ....	100 2.71
91. Andesite, summit of Mt. Orizaba, Mexico, 18,300 ft. altitude. Unquestionably a lava, and not a tuff, somewhat porous, giving off bubbles when immersed in water.	P. ct. Vol.	.... ....	67.07 .22	16.28 .05	2.46 .00	3.94 .01	10.25 .03	.... ....	100 .31
492. Amphibolite, Chester, Mass. A very coarse-grained specimen. Walker Museum.	P. ct. Vol.	.... ....	36.59 2.20	17.13 1.05	1.57 .09	42.93 2.59	1.78 .10	.... ....	100 6.03
492a. As the gas was still coming off slowly at the end of 5 hours, the same material was heated the next day for an additional 3½ hours.	P. ct. Vol.	.... ....	7.55 .03	13.65 .05	4.62 .01	66.96 .25	7.22 .03	.... ....	100 .37

Specimen No. and remarks.	Per cent or volume.	Hydrogen sulphide (H <sub>2</sub> S).	Sulphur dioxide (SO <sub>2</sub> ).	Carbon dioxide (CO <sub>2</sub> ).	Carbon monoxide (CO).	Methane (CH <sub>4</sub> ).	Hydrogen (H <sub>2</sub> ).	Nitrogen (N <sub>2</sub> ).	Helium (He).	Total.
93. Pitchblende, Beaver Co., Colo. From H. N. McCoy.	P. ct. Vol.	.... ....	( <sup>5</sup> ) ....	( <sup>6</sup> ) ....	23.94 .24	2.57 .03	7.16 .07	27.85 .27	38.48 .37	100 .98
794. Carnotite, Colorado, from H. N. McCoy. Uranyl vanadate, probably with some radium.	P. ct. Vol.	trace 0.00	.... ....	81.31 2.46	7.74 .23	.71 .02	1.48 .05	7.48 .22	1.28 .04	100 3.02
95. Greenalite rock, Biwabik formation, Mesabi district, Minn. No. 45759 U. S. G. S. From C. K. Leith.	P. ct. Vol.	.17 .01	.... ....	7.02 .42	4.03 .24	.04 .00	86.28 5.18	2.46 .14	.... ....	100 5.99
96. Grünerite rock, Mesabi district, Minn. A ferruginous chert. No. 45113 U. S. G. S. From Dr. Leith.	P. ct. Vol.	.68 .02	.... ....	37.97 1.14	8.57 .26	.78 .02	45.78 1.39	6.22 .19	.... ....	100 3.02
97. Micaceous quartzite, Uinta Mts., Utah. From Dr. Leith.	P. ct. Vol.	.36 .01	.... ....	40.44 .57	8.62 .12	2.46 .03	43.93 .63	4.19 .06	.... ....	100 1.42

<sup>1</sup>In order to see whether the methane came from hydrocarbons soluble in alcohol or ether, this material, after being very finely pulverized, was digested with alcohol (free from organic impurities) for 20 hours; then with fat-free ether for 45 hours. It was then thoroughly washed with ether on a filter which had previously been treated with the same fat-free ether. Afterwards dried at 100° in an oven.

<sup>2</sup>To get rid of all carbonates the powder was treated with concentrated nitric acid for 66 hours. Much gas was given off, including a copious evolution of nitric oxide. The powder was washed until all traces of acid were removed, after which it was dried in an air-bath at 115°. This material heated then gave No. 87.

<sup>3</sup>Treated with dilute sulphuric acid for three days in a vacuum. The powder was washed on a filter until the filtrate was no longer made turbid by barium chloride, and then dried in an oven and heated in an air-bath at 125° for over an hour.

<sup>4</sup>Nos. 92 and 92a. A perfect vacuum was maintained between these two combustions.

<sup>5</sup>Sulphate.

<sup>6</sup>Carbonated.

<sup>7</sup>The high percentage of nitrogen shown in this analysis is not due to leakage of air, for the pump held its vacuum for days afterwards during the spectroscopic examinations. The yellow helium line, D<sub>3</sub> (λ = 5876) stood forth brilliantly, but no argon lines could be seen in the spectrum.



TABLE 8—Continued.

Specimen No. and remarks.	P. ct. or vol.	H <sub>2</sub> S.	SO <sub>2</sub> .	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	NH <sub>3</sub> .	Total.
98. Quartzite, Rib Hill, near Wausau, Wis. From Samuel Weidman. Famous for its gas bubbles. Powdered on an anvil and metallic iron thus introduced removed as completely as possible with a magnet.	P. ct. Vol.	0.52 .01	.... ....	68.15 .62	6.87 .06	2.52 .02	19.53 .17	2.41 .02	.... ....	100 .90
199. Quartzite, Rib Hill, Wis. Same specimen as No. 98. Granules used instead of fine powder. Crumbles readily into granules, which were treated with boiling hydrochloric acid to remove any iron which might have come from the anvil.	P. ct. Vol.	.17 .00	.... ....	96.69 .86	.96 .01	.23 .00	1.39 .02	.56 .00	.... ....	100 .89
100. Auriferous, pyritiferous quartz, Cargo, near Orange, New South Wales. No. 837 N. S. W.; No. 3150 U. of W. Dr. Leith. Reduced to a coarse powder on an anvil and treated with boiling dilute hydrochloric acid which removed any iron introduced. After being carefully washed and dried it was more finely reduced in a porcelain mortar.	P. ct. Vol.	1.07 .01	.... ....	75.54 .66	3.36 .03	3.99 .04	13.57 .12	2.47 .02	.... ....	100 .88
101. Beryl from pegmatite dike, New England. Walker Museum Collection. Material for this analysis taken from a massive beryl, 8 inches in diameter, as transparent as window-glass and without visible inclusions or impurities. Instead of being pulverized the material was used in the form of small fragments which were washed with boiling hydrochloric acid. After heating, the transparent fragments became white and opaque, resembling porcelain.	P. ct. Vol.	.34 .00	.... ....	35.05 .15	3.37 .01	1.37 .00	55.83 .24	4.04 .02	.... ....	100 .42
101a. As $\frac{1}{4}$ hours failed to expel all the gas, the vacuum was maintained overnight, and the material heated 4 hours more next day.	P. ct. Vol.	.... ....	.... ....	10.0 .01	2.2 .00	5.6 .00	76.9 .07	5.3 .00	.... ....	100 .08
102. Pegmatite, containing many crystals of tourmaline, Chesterfield, Mass. Walker Museum.	P. ct. Vol.	.04 .00	.... ....	3.70 .06	3.53 .06	3.03 .05	87.21 1.45	2.42 .04	0.07 .00	100 1.66
103. Quartz from pegmatite vein, Jones Falls, Baltimore, Md. No. 221, Univ. of Wis. collection. Dr. Leith. Specimen contained a large crystal of microcline over 2 inches in length, indicating conditions favorable to crystallization. No microcline was used for the analysis, however. If pegmatites contain much gas, it was thought this one should yield a good volume.	P. ct. Vol.	.... ....	.... ....	68.4 .09	13.9 .02	2.9 .00	7.4 .01	7.4 .01	.... ....	100 .13
104. Albite, Gibb's mica mine, Yancey Co., N. C. Walker Museum.	P. ct. Vol.	.... ....	.... ....	9.3 .00	11.3 .01	19.6 .02	59.8 .04	.... ....	.... ....	100 .07
105. Quartz from Miocene lava, Iron Co., Utah. No. 46614 U. S. G. S. From E. C. Harder.	P. ct. Vol.	.22 .00	.... ....	57.71 .12	27.12 .05	2.32 .00	12.63 .03	.... ....	.... ....	100 .20
<sup>2</sup> 106. Allegan meteorite, a stony aerolite which fell at Allegan, Mich., July 10, 1899, and was dug out of the sand still hot, within 5 minutes of its fall. From U. S. National Museum through G. P. Merrill. Described by Merrill and Stokes (Proc. Washington Academy of Sciences, vol. 2, pp. 41-68). Before extracting the gas, the powdered meteoric material was heated in a vacuum at 150° for 3 hours in the presence of phosphorus pentoxide. Apparatus was then allowed to stand for 20 hours to enable the drying agent to absorb all moisture not chemically combined.	P. ct. Vol.	trace .00	.... ....	41.74 .21	38.61 .19	2.92 .01	16.73 .08	.00 .00	.... ....	100 .49

<sup>1</sup>The volume of carbon dioxide being much greater in the case of the granules than in the finely reduced powder strongly suggests that much of this gas is mechanically inclosed in cavities within the quartzite, and escapes when the granules are pulverized. This opinion was strengthened by a slight cracking noise which came from within the tube as soon as heat was applied. The gas came off with a rush when the tube was heated.

<sup>2</sup>No. 106. Chemical analysis by Dr. H. N. Stokes: Metallic part, .306 per cent., as follows: Fe, 21.09; Cu, .01; Ni, 1.81; Co, .15. Stony part, 76.91 per cent., as follows: SiO<sub>2</sub>, 34.95; TiO<sub>2</sub>, .08; P<sub>2</sub>O<sub>5</sub>, .27; Al<sub>2</sub>O<sub>3</sub>, 2.55; Cr<sub>2</sub>O<sub>3</sub>, .53; FeO, 8.47; FeS, 5.05; MnO, .18; CaO, 1.73; MgO, 21.99; K<sub>2</sub>O, .23; Na<sub>2</sub>O, .66; H<sub>2</sub>O at 110°, .06; above 110°, .19; 100.00.

TABLE 8—Concluded.

Specimen No. and remarks.	P. ct. or vol.	H <sub>2</sub> S.	SO <sub>2</sub> .	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	NH <sub>3</sub> .	Total.
1107. Estacado meteorite, fell near Estacado, Tex., in 1882. Described by K. S. Howard (Am. Jour. Sci., vol. 22 (1906), pp. 55-60). Kept in a vacuum at ordinary temperature with phosphorus pentoxide for 66 hours; then heated at 150° for 5 hours, and allowed to remain in vacuo for 19 hours more, before attempting to extract the gas.	P. ct. Vol.	0.39 .00	.... ....	28.47 .24	29.31 .25	3.39 .03	36.25 .31	1.69 .01	.... ....	100 .81
1108. Toluca meteorite, a medium octahedrite from Toluca, Mexico.										
<sup>3</sup> First determination.....	P. ct. Vol.	.02 .00	.... ....	43.29 10.57	35.48 8.67	1.44 .35	17.84 4.36	1.93 .47	.... ....	100 24.42
<sup>4</sup> Second determination.....	P. ct. Vol.	.10 .01	.... ....	22.32 2.25	53.99 5.45	1.91 .19	18.49 1.87	3.19 .32	.... ....	100 10.09
<sup>5</sup> Third determination.....	P. ct. Vol.	.13 .00	.... ....	6.40 .12	71.05 1.32	2.35 .04	14.54 .27	5.53 .10	.... ....	100 1.85
1109. Iron ore, Iron Co., Utah, No.—, U. S. G. S. From C. K. Leith. Chiefly limonite and magnetite, with some iron carbonate and sulphate:										
First portion (gas which came off in 20 minutes).	P. ct. Vol.	.... ....	51.35 11.55	20.62 4.64	27.95 6.15	.68 .15	.... ....	.... ....	.... ....	100 22.49
Second portion (gas which came off in the next 40 minutes).	P. ct. Vol.	.... ....	48.75 10.65	20.43 4.47	30.12 6.58	.03 .00	.44 .10	.23 .05	.... ....	100 21.85
Third portion (material heated 3 hours more).	P. ct. Vol.	.... ....	51.40 1.72	14.92 .50	33.28 1.12	.40 .01	.... ....	.... ....	.... ....	100 3.35
1110. Basaltic lava, Kilauea, Hawaii, Cascade of 1863. A rather porous lava, having a specific gravity of only 2.00.	P. ct. Vol.	.88 .01	.... ....	70.42 .60	21.41 .18	2.49 .02	2.01 .02	2.79 .02	.... ....	100 .85
1111. Fresh lava, Vesuvius, from the lava stream of April, 1906, collected by F. B. Taylor, March 30, 1907. From south side of a quarry in front of the church in Bosco Trecase, above Torre Annunziata. This specimen came from 10 ft. below the top and 2½ ft. from the bottom of the flow, which had been blasted at this point.	P. ct. Vol.	8.86 .03	.... ....	73.22 .31	12.24 .05	2.33 .01	1.47 .01	1.88 .01	.... ....	100 .42
1112. Fresh lava, Vesuvius, same flow as last; 0.5 kilometer SE. of church where No. 1111 was collected. About 8 ft. below surface and 2 ft. from bottom of bed. Collected March 30, 1907, by F. Taylor.	P. ct. Vol.	23.43 .14	.... ....	63.49 .39	7.94 .05	2.33 .02	1.50 .01	1.31 .01	.... ....	100 .62

<sup>1</sup>No. 107. Chemical analysis by J. M. Davison: Fe, 14.68; Ni, 1.60; Co, .08; S, 1.37; P, .15; SiO<sub>2</sub>, 35.82; FeO, 15.53; MgO, 22.74; CaO, 2.99; Al<sub>2</sub>O<sub>3</sub>, 3.60; Na<sub>2</sub>O, 2.07; K<sub>2</sub>O, .32; 100.95.

<sup>2</sup>No. 108. Average of 13 analyses compiled by Farrington (Pub. Field Columbian Museum No. 120, pp. 82-84): Fe, 89.66; Ni, 7.90; Co, 0.63; P, 0.24; S, 0.14; Si, 0.02; Misc., 0.57; 99.16.

<sup>3</sup>Iron borings and filings were used, but with these there was included a little rust, which adhered to the metal when it was withdrawn with a magnet.

<sup>4</sup>The material used in this determination consisted of bright borings carefully freed from rust, a pocket of which unfortunately was encountered in drilling. But in spite of much care exercised in drawing out the metallic borings with a magnet, some rust adhered to them and consequently was heated with the metal in the combustion tube. However, this amounted to much less than in the first determination. No filings were used.

<sup>5</sup>For this determination borings from the interior of the specimen were carefully made by Wm. Gaertner & Co., scientific-instrument makers. There was no visible rust adhering to these borings, which were then worked twice, with a magnet, without any impurities being left behind. The white paper on which this operation was performed failed to show the slightest discoloration, such as it had done in the two previous determinations. As usual the material was heated at 100° for 3 hours, in the presence of P<sub>2</sub>O<sub>5</sub>, and then allowed to stand in the vacuum overnight to remove all free moisture. Though the vacuum was perfect at the end of this time, the first two pumpings of gas (amounting to 0.2 cubic centimeter) which were evolved when heat was applied, were not kept, since it was desired to eliminate atmospheric air as a source of nitrogen.

A comparison of the three determinations, No. 108 shows what a tremendous effect the presence of a little iron rust will have upon the gases evolved from a metallic meteorite. Much of this gas is doubtless derived from iron carbonate and the hydrated oxide of iron, as will be explained under the topic of gas due to chemical reactions. Great care is therefore necessary in making gas analysis of iron meteorites to avoid any contamination of rust.

<sup>6</sup>The most striking feature of these analyses is the unusual amount of sulphur dioxide, which indicates an oxidized condition of the ore.

<sup>7</sup>The odor of sulphur dioxide was very prominent in the gas obtained from these two Vesuvian lavas.

## GROUPINGS AND CLASSIFICATIONS OF ANALYSES.

As the volumes and relative proportions of the gases found in the foregoing analyses vary within wide limits, the nature of this variation can best be shown by grouping the results. To make these tables as complete as possible, not only the results of the present studies, but all the available analyses of other investigators, have been included in the lists. Except in the case of four of the five analyses by Tilden, relative to which sufficient data are not given, all of the figures in these tables refer to volumes of gas per volume of rock. Previous investigators have usually given the total volume of gas and the percentages of each constituent. From these I have calculated the volumes for each individual gas.

TABLE 9.—Analyses classified by groups of rocks.

No.	Rock and locality.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.	Analyst.
<i>Granites and gneisses of igneous origin.</i>									
	Granite, Skye (p. ct.).....	.....	28.60	6.45	3.02	61.68	5.13	99.88	Tilden.
	Granite, Vire (average).....	0.05	.86	.35	.12	5.29	.04	6.71	Gautier.
	Granitoid porphyry, L'Estere.....		4.50	.32	.19	2.36	.16	7.53	Do
1	Medium-grained, white granite.....		.28	.07	.07	.92	.10	1.44	Chamberlin.
2	Coarse-grained, reddish granite.....		.42	.09	.10	2.94	.11	3.66	Do
4	Laurentian gneiss, Ontario.....		.31	.08	.06	1.50	.13	2.08	Do
9	Pike's Peak granite.....		.37	.05	.02	.04	.12	.60	Do
19	Granite porphyry, Menominee.....		3.51	.72	.06	2.34	.22	6.85	Do
20	Fine-grained gneiss, Menominee.....	tr.	1.89	.23	.02	.43	.23	2.80	Do
21	Fine-grained banded gneiss, Menominee.....		6.63	1.13	.06	1.37	.08	9.27	Do
22	Laurentian granite, Marquette.....		1.89	.13	.03	.74	.15	2.94	Do
24	Pink granite, North Carolina.....	tr.	.16	.05	.02	.38	.04	.65	Do
25	Gray granite, Quincy, Mass.....	tr.	.39	.09	.06	1.04	.02	1.60	Do
26	Gray granite, Russia.....	tr.	1.79	.18	.....	.99	.....	2.96	Do
33	Laurentian gneiss, Marquette.....	tr.	.85	.15	.07	1.79	.12	2.98	Do
37	Oglesby blue granite, Georgia.....	tr.	1.13	.11	.03	1.06	.05	2.38	Do
38	Stone Mountain granite, Georgia.....	tr.	.08	.03	.01	.60	.04	.76	Do
39	Ortonville granite, Minn.....	tr.	1.20	.05	.01	.05	.05	1.36	Do
57	Granite porphyry boulder, New York.....	.04	carb.	.27	.02	.85	.04	1.22	Do
66	Gneiss of igneous origin, Ontario.....	tr.	.28	.13	.03	.95	.08	1.47	Do
	Average of 19 analyses.....	tr.	1.47	.22	.05	1.36	.09	3.19	
<i>The syenite group.</i>									
44	Nephelite syenite, Ontario.....	.....	0.29	0.05	0.04	0.25	0.05	0.68	Chamberlin.
51	Shonkinite, Highwood Mountains, Mont.....	tr.	.11	.06	.05	.95	.05	1.22	Do
53	Quartz syenite porphyry, Colorado.....	.....	carb.	.11	.08	.22	.03	.44	Do
56	Hornblende syenite, Maine.....	tr.	.15	.07	.03	2.22	.03	2.50	Do
	Average of 4 analyses.....	tr.	.18	.07	.05	.91	.04	1.25	
<i>The gabbro-diorite group.</i>									
	Gabbro, Lizard, England (p. ct.).....	.....	5.50	2.16	2.03	88.42	1.90	100.01	Tilden.
15	Gabbro, Isle of Skye.....	.....	.00	.00	.....	1.40	.....	1.40	Travers.
	Gabbro-diorite, Mt. Sneffels, Colo.....	.....	.40	.10	.04	1.13	.14	1.81	Chamberlin.
16	Gabbro, summit of Mt. Sneffels.....	.....	carb.	.12	.02	.97	.12	1.23	Do
17	Orthoclase gabbro, Duluth.....	.....	.44	.12	.07	2.68	.33	3.64	Do
32	Schistose gabbro, Menominee.....	.02	20.07	.58	.20	8.54	.32	29.73	Do
36	Olivine gabbro, Duluth.....	tr.	.16	.07	.04	.52	.05	.84	Do
52	Theralite, Crazy Mountains, Mont.....	tr.	1.08	.17	.04	.93	.03	2.25	Do
55	Intrusive, Highwood Mountains, Mont.....	.....	.28	.07	.04	.45	.03	.87	Do
60	Diorite plug in shales, Colorado.....	.03	.22	.06	.05	1.10	.06	1.52	Do
73	Coarse diorite boulder, Maine.....	.06	.27	.07	.04	1.29	.05	1.78	Do
74	Diorite, Penobscot Bay, Me.....	.07	.21	.04	.20	3.95	.14	4.61	Do
	Average of 11 analyses.....	.02	2.31	.13	.07	2.09	.11	4.73	
<i>Diabases and basalts.</i>									
	Basalt, Antrim.....	.....	2.57	1.61	0.80	2.89	.13	8.00	Tilden.
	Ophite, Villefranche (average).....	.24	2.39	.33	.08	4.52	.02	7.58	Gautier.
	Lherzolite, Lherz.....	1.86	12.29	.31	tr.	1.15	tr.	15.61	Do
11	Keweenaw diabase, Wisconsin.....	.....	.59	.05	.19	3.83	.25	4.91	Chamberlin.
34	Keewatin greenstone, Mesabi.....	.19	20.08	1.16	.09	10.10	.57	32.19	Do

TABLE 9.—Analyses classified by groups of rocks.—Continued.

No.	Rock and locality.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.	Analyst.
<i>Diabases and basalts</i> —Cont.									
35	Keweenaw diabase, Minnesota.....	0.01	0.25	0.06	0.06	3.15	0.06	3.59	Chamberlin.
45	Iron basalt, Greenland.....	tr.	3.74	1.74	.17	2.24	.16	8.05	Do
50	Nephelite melilitite basalt, Texas.....	.05	1.07	.20	.06	1.16	.10	2.64	Do
61	Diabase, Nahant, Mass.....	.19	4.91	.21	.12	3.13	.15	8.71	Do
84	Vogesite, La Plata, Colo.....	carb.	.14	.03	1.08	.05	1.30	Do	Do
85	Keweenaw diabase, Michigan.....	tr.	1.31	.09	.09	2.34	.05	3.88	Do
110	Basalt of 1868, Kilauea, Hawaii.....	.01	.60	.18	.02	.02	.02	.85	Do
111	Lava of 1906, Vesuvius.....	.03	.31	.05	.01	.01	.01	.42	Do
112	Lava of 1906, Vesuvius.....	.14	.39	.05	.02	.01	.01	.62	Do
	Average of 14 analyses.....	.19	3.96	.44	.12	2.54	.11	7.36	
<i>Andesites.</i>									
13	Andesite, Ouray Co., Colo.....	carb.	.09	.02	.08	.08	.27	Chamberlin.	
47	Andesite, Red Mountain, Ariz.....	tr.	5.12	.57	.30	.12	.26	6.37	Do
62	Andesite, Rosita Hills, Colo.....	carb.	.27	.05	.30	.13	.75	Do	
64	Andesite, Lipari Islands.....	tr.	.56	.04	.01	.17	.02	.80	Do
70	Andesite, Granite Mountain, Utah.....	tr.	2.66	.16	.03	.53	.05	3.43	Do
72	Phonolite trachyte, Pike's Peak.....	tr.	.76	.05	.03	.19	.06	1.08	Do
91	Andesite, summit of Orizaba.....	....	.22	.05	.00	.01	.03	.31	Do
	Average of 9 analyses.....	....	1.86	.18	.06	.20	.09	2.39	
<i>Rhyolites.</i>									
10	Rhyolite, Marble Mountain, Arizona....	....	.22	.08	.04	.03	.13	.50	Chamberlin.
49	Rhyolite vitrophyre, Telluride.....	....	2.33	.05	.03	.07	.03	2.51	Do
	Pitchstone rhyolite, Rosita Hills.....	....	.07	....	.13	....	.20	Do	
59	Nevadite, Chalk Mountain, Colo.....	....	.15	.06	.01	.02	.03	.27	Do
	Average of 4 analyses.....	....	.69	.05	.02	.06	.05	.87	
<i>Schists.</i>									
3	Keewatin schist, Mesabi.....	....	7.67	.28	.05	3.81	.22	12.03	Chamberlin.
23	Schist with chloritoid, Black Hills.....	....	.46	.10	.04	3.07	.05	3.72	Do
	Average.....	....	4.06	.19	.05	3.44	.13	7.87	
<i>Miscellaneous porphyries.</i>									
14	Coarse porphyry, Ouray Co., Colo.....	carb.	.05	.02	.22	.01	.30	Chamberlin.	
78	Topaz quartz-porphyry, Saxony.....	....	.32	.08	.05	.44	.08	.97	Do
	Average.....	....	.32	.06	.04	.33	.04	.79	
<i>Quartz.</i>									
71	Smoky quartz, Branchville, Conn.....	tr.	.07	.00	.00	.00	tr.	.07	Wright.
83	Vein quartz, Iron Co., Utah.....	....	.11	.09	.03	.53	.05	.81	Chamberlin.
100	Crystals (aqueous origin), North Carolina.	tr.	.03	tr.	tr.	.01	.03	.08	Do
103	Auriferous quartz, New South Wales.....	.01	.66	.03	.04	.12	.02	.88	Do
105	Quartz from pegmatite, Baltimore.....	....	.09	.02	tr.	.01	.01	.13	Do
	Quartz from lava, Utah.....	tr.	.12	.05	.00	tr.	.03	.20	Do
	Average of 6 analyses.....	....	.18	.03	.01	.11	.02	.35	
<i>Metamorphosed sedimentaries.</i>									
	Pyroxene gneiss, Ceylon (p. ct.).....	....	77.72	8.06	0.56	12.49	1.16	99.99	Tilden.
	Gneiss, Seringapatam (p. ct.).....	....	81.62	5.36	.51	61.93	0.56	99.98	Do
27	Baltimore gneiss, Bryn Mawr, Pa.....	tr.	.13	.10	.14	4.32	.04	4.73	Chamberlin.
28	Baltimore gneiss, Schuylkill River.....	.30	1.35	.22	.11	4.02	.10	6.10	Do
29	Wissahickon mica gneiss, Pennsylvania.....	tr.	.19	.07	.02	.65	.04	.97	Do
30	Wissahickon gneiss, Schuylkill River.....	tr.	.19	.08	.08	1.90	.08	2.33	Do
31	Cambrian gneiss, Coatesville, Pa.....	....	.26	.09	.01	.37	.03	.76	Do
43	Sillimanite gneiss, Quebec.....	{ SO <sub>2</sub> }	2.05	.09	.03	.05	.07	5.05	Do
54	Altered Jurassic shale, Colorado.....	tr.	carb.	.15	.04	.45	.04	.68	Do
55	Garnetiferous gneiss, Quebec.....	.11	.16	.07	.02	.41	.02	.79	Do
65	Fine-grained gneiss, Ontario.....	{ SO <sub>2</sub> }	.68	....	.05	....	4.88	Do	
67	Feather amphibolite, Ontario.....	tr.	carb.	.48	.03	.32	.06	.90	Do
68	Amphibolite, Ontario.....	tr.	carb.	.26	.05	2.01	.06	2.31	Do
69	Rice Rock, Sudbury, Ontario.....	16	.47	.16	.05	2.32	.06	3.22	Do
92	Amphibolite, Chester, Mass.....	....	2.23	1.10	.10	2.84	.13	6.40	Do
	Average of 13 analyses.....	.57	.77	.22	.05	1.52	.05	3.18	



TABLE 9.—*Analyses classified by groups of rocks.*—Concluded.

No.	Rock and locality.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.	Analyst.
<i>Shales.</i> <sup>1</sup>									
5	Kinderhook shale, Burlington, Iowa	....	9.28	0.35	0.12	0.22	0.15	10.12	Chamberlin.
6	Portage shale, Ithaca, N. Y.	....	1.47	.83	.16	1.23	leak	3.69	Do
18	Hamilton shale, Marysville, Pa.	tr.	.41	.17	.07	1.45	.40	2.50	Do
41	Hamilton shale, Nashville, Tenn.	29.38	20.10	4.38	....	37.03	....	90.89	Do
42	Oil shale, Platteville, Wis.	3.90	10.43	4.82	20.67	7.57	1.26	48.65	Do
	Average of first 3 analyses	....	3.75	.45	.11	.97	.18	5.43	
<i>Sandstones and quartzites.</i>									
8	Potsdam sandstone, Baraboo, Wis.	....	.47	.18	....	.01	.38	1.01	Chamberlin.
12	Quartzite schist, Baraboo, Wis.	....	.16	.07	.03	.03	.06	.35	Do
75	Potsdam sandstone, Ablemans, Wis.	tr.	.09	.05	.02	.13	.05	.34	Do
76	Same as last, powdered and reheated	tr.	.05	.07	.02	.23	.08	.45	Do
77	Huronian quartzite, Baraboo, Wis.	tr.	.11	.04	.01	.24	.03	.43	Do
78	Red Beds, Colorado City	tr.	carb.	.71	.07	.32	.06	1.16	Do
80	St. Peter sandstone, Minnehaha Falls	tr.	.02	tr.	.01	tr.	.01	.04	Do
81	Same as last, powdered and reheated	....	.03	.07	.01	tr.	.21	.49	Do
82	Quartzite, Grenville series, Quebec	.23	.21	.04	.01	.09	.01	.59	Do
97	Micaceous quartzite, Uinta Mountains	.01	.57	.12	.03	.63	.06	1.42	Do
98	Quartzite, Rib Hill, Wis.	.01	.62	.06	.02	.17	.02	.90	Do
99	Same as last, granules used	tr.	.86	.01	tr.	.02	tr.	.89	Do
	Average of 12 analyses	.02	.29	.11	.02	.17	.08	.69	

<sup>1</sup>The two bituminous shales which derived the bulk of their gas from the distillation and decomposition of organic matter are necessarily omitted from the average.

TABLE 10.—*Various minerals.*

No.	Mineral and locality.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	H <sub>2</sub> .	CH <sub>4</sub> .	N <sub>2</sub> .	A + He.	Total.	Analyst.
	Feldspar	....	1.20	0.01	0.03	0.01	0.02	....	1.27	Dewar.
	Celestial graphite	....	6.66	....	.18	.39	tr.	....	7.25	Do
	Graphite, Borrodale	....	.95	.20	.58	.68	.17	....	2.60	Do
	Chlorite, Zoptan, Moravia	....	.33	1.33	5.84	....	....	....	7.50	Travers.
	Serpentine, Zermatt	....	....	....	2.08	....	....	....	2.08	Do
	Mica, Westchester, Pa.	....	.42	.22	....	....	....	....	.64	Do
	Talc, Greiner, Tyrol	....	.19	.11	....	....	....	....	.30	Do
	Feldspar, Peterhead granite	....	3.08	.55	....	....	....	....	3.63	Do
	Malacoe	....	1.55	....	.03	....	.02	.17	1.77	Kitchin and Winterson.
7	Muscovite, Canada	....	1.26	.12	.10	.04	.27	....	1.79	Chamberlin.
40	Biotite, Ortonville granite	0.22	12.45	.23	.30	.06	.21	....	13.47	Do
48	Pyroxene crystals, Red Mountain	.10	.69	.16	.08	.01	.06	....	1.10	Do
63	Anorthosite, Quebec	tr.	2.36	.27	.56	.02	.06	....	3.27	Do
90	Wollastonite, Lewis Co., N. Y.	....	2.37	.18	.06	.02	.08	....	2.71	Do
93	Pitchblende, Beaver Co., Colo.	sul.	carb.	.24	.07	.03	.27	.37	.98	Do
94	Carnotite	tr.	2.46	.23	.05	.02	.22	.04	3.02	Do
95	Greenalite rock, Mesabi	tr.	.42	.24	5.18	tr.	.15	....	5.99	Do
96	Grünerite rock, Mesabi	.02	1.14	.26	1.39	.02	.19	....	3.02	Do
101	Beryl, pegmatite, New England	tr.	.16	.01	.31	.01	.02	....	.50	Do
102	Pegmatite with tourmaline	tr.	.06	.06	1.45	.05	.04	....	1.66	Do
104	Albite, Yancey Co., N. C.	tr.	tr.	.01	.04	.02	....	....	.07	Do
	Average of 21 analyses	.02	1.88	.19	.92	.06	.08	.03	3.18	

It should, perhaps, be stated that in making this and other averages of analyses, in those cases where, on account of excessive carbonation, no figures are given for carbon dioxide, the average amount of this gas calculated from the other analyses is assumed to be present in those rocks marked "carbonated." This addition is added to the average total and makes this figure slightly greater than the average of the column which it foots. The same method has been used for carbon monoxide in the three of Travers's analyses where carbon monoxide and hydrogen are put together.

TABLE 11.—*Stony meteorites.*

No.	Meteorite.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.	Analyst.
	Guernsey, Ohio .....	....	1.80	0.13	0.06	0.95	0.05	2.99	Wright.
	Pultusk, Poland .....	....	1.06	.06	.06	.52	.04	1.75	Do
	Parnallee, India .....	....	2.13	.04	.05	.36	.04	2.63	Do
	Weston, Conn. ....	....	2.83	.08	.04	.46	.08	3.49	Do
	Iowa County, Iowa .....	....	.88	.05	....	1.45	.12	2.50	Do
	Kold Bokkeveld .....	....	23.49	.61	.82	.10	.21	25.23	Do
	Dhurmsala, India. ....	....	1.59	.03	.10	.74	.03	2.51	Dewar.
	Pultusk, Poland .....	....	2.34	.19	.27	.64	.09	3.54	Do
	Mocs .....	....	1.25	.07	.09	.45	.07	1.94	Do
	Orgueil .....	{ SO <sub>2</sub> 48.03 }	7.40	1.14	.87	....	.33	57.87	Do
106	Allegan, Mich. ....	tr.	.21	.19	.01	.08	tr.	.49	Chamberlin.
107	Estacado, Texas .....	tr.	.24	.25	.03	.31	.01	.84	Do
	Average of 12 analyses .....	4.00	3.77	.24	.20	.50	.09	8.80	

The figures for the Orgueil meteorite which yielded such a remarkable amount of sulphur dioxide make the average for the sulphur gases an abnormal one. The presence of this gas in quantity must mean that the meteorite has suffered much from weathering and oxidation subsequent to its fall. Considerable troilite has passed into iron sulphate which has been decomposed by the heat of the combustion-furnace.

Omitting the sulphur dioxide of this specimen, the average total volume of gas from stony meteorites is reduced to 4.80 times the volume of the meteoritic material.

TABLE 12.—*Iron meteorites.*

No.	Meteorite.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.	Analyst.
	Lenarto .....	....	0.13	0.00	....	2.44	0.28	2.85	Graham.
	Augusta Co., Va. ....	....	.31	1.21	....	1.14	.51	3.17	Mallet.
	Tazewell Co., Tenn. ....	....	.46	1.31	....	1.35	.05	3.17	Wright.
	Shingle Springs, Cal. ....	....	.13	.12	....	.67	....	.97	Do
	Cross Timbers, Tex. ....	....	.11	.19	....	.99	....	1.29	Do
	Dickson County, Tex. ....	....	.29	.34	....	1.57	....	2.20	Do
	Arva, Hungary .....	....	5.92	31.91	....	8.57	.73	47.13	Do
	Cranbourne, Australia .....	....	.04	1.13	0.16	1.63	.63	3.59	Flight. <sup>1</sup>
	Rowton, Shropshire .....	....	.33	.47	....	4.96	.62	6.38	Do
108	Toluca, Mexico .....	tr.	.12	1.32	.04	.27	.10	1.85	Chamberlin.
	Average .....	....	.78	3.80	.02	2.36	.30	7.26	
	Average omitting Arva meteorite. ....	....	.21	.67	.02	1.67	.24	2.83	

<sup>1</sup> Flight, Phil. Trans. No. 172 (1882), pp. 893-894 and p. 896.

Methane was determined in only two of these analyses. In these two it averaged 0.10 volume; but in order to make the figures consistent in the table, it was necessary to average these as if the eight other meteorites yielded no marsh-gas, though it is highly probable that this gas was present and has been included in the figures given for hydrogen.

The unusual amount of gas from the Arva specimen recalls the behavior of the Toluca meteorite,<sup>1</sup> which, at the first attempt, produced 24.42 volumes of gas, owing to the presence of a small quantity of iron rust, but whose pure metal evolved only 1.85 volumes. An average, omitting the Arva, is therefore made.

<sup>1</sup> Ante, p. 22.

## AVERAGES OF THE GROUPS.

TABLE 13.—*Igneous rocks.*

Order.	Type of rock.	No. of analyses.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
1	Basic schists .....	2	0.00	4.06	0.19	0.05	3.44	0.13	7.87
2	Diabases and basalts. ....	14	.19	3.96	.14	.12	2.54	.11	7.36
3	Gabbros and diorites. ....	11	.02	2.31	.13	.07	2.09	.11	4.73
4	Granites and gneisses. ....	19	.00	1.47	.22	.05	1.36	.09	3.19
5	Andesites .....	7	.00	1.86	.18	.06	.20	.09	2.39
6	Syenites .....	4	.00	.18	.07	.05	.91	.04	1.25
7	Rhyolites .....	4	.00	.69	.05	.02	.06	.05	.87
8	Miscellaneous porphyries. ....	2	.00	.32	.06	.04	.33	.04	.79

The general averages bring out the fact that, while rocks of each group may vary considerably among themselves, each group as a whole fits into a logical place in relation to the other groups. The established order appears to be, most gas from those rocks which contain the greatest proportion of ferromagnesian minerals. Though much influenced by other conditions, such as relative age and nature of the igneous mass, the general deduction may be made that the volume of gas obtained from rocks varies, in a rough way, in proportion to the percentage of ferromagnesian minerals present. Diabases, basalts, and basic schists take first rank in the quantity of gas evolved. Next to them appear diorites and gabbros which are also near the basic end, but formed under different conditions. Andesites are out of their place in this list, as they take precedence over granites in the proportion of ferromagnesian minerals, but these andesites were all either of Tertiary or Recent age, whereas most of the granites came from Pre-Cambrian formations, and, as the next table will show, ancient igneous rocks yield more gas than modern ones. The rhyolites, which combine a scarcity of basic minerals with Tertiary age, foot the list.

It is to be noted that the rank of a type of rock on the basis of an individual gas does not in all cases correspond to its rank for some other gas, or in respect to total volumes. The andesites tested gave more carbon dioxide than either the granites or the syenites, though both of these types greatly surpassed the andesites in the matter of hydrogen. But this involves another factor: in deep-seated rocks, hydrogen and carbon dioxide are of about equal importance; in surface flows, carbon dioxide predominates. Though carbon monoxide and methane are somewhat variable, the minor gases generally increase or decrease with the total volumes.

TABLE 14.—*Rocks of sedimentary origin.*

Order.	Type of rock.	No. of analyses.	Sulphur gases.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
1	Shales (non-bituminous) .....	3	0.00	3.72	0.45	0.11	0.97	0.18	5.43
2	Metamorphosed sediments .....	13	.57	.77	.22	.05	1.52	.05	3.18
3	Sandstones and quartzites .....	12	.02	.29	.11	.02	.17	.08	.69

Among sedimentary rocks, sandstones and quartzites yield less gas than shales, while the metamorphic group, comprising both altered shales and sandstones, together with modified limestones, take an intermediate position, though they surpass shales in hydrogen and the sulphur gases.

TABLE 15.—*Meteorites.*

Order.	Type of meteorite.	No. of analyses.	Sulphur gases.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
1	Stony .....	12	4.00	3.77	0.24	0.20	0.50	0.09	8.80
	Without SO <sub>2</sub> of Orgueil .....	12	.00	3.77	.24	.20	.50	.09	4.80
2	Iron .....	10	.00	.78	3.80	.02	2.36	.30	7.26
	Neglecting Arva .....	9	.00	.21	.67	.02	1.67	.24	2.83

A comparison of the two types of meteorites indicates that carbon dioxide is much more important in the gas from stony specimens than in that from the metallic bodies, but that iron meteorites yield several times as much carbon monoxide and hydrogen as do the stones. Sufficient data are not at hand to permit a comparison of the amount of marsh-gas from these two types; nitrogen, however, appears to come in greater volume from the iron meteorites.

ANALYSES CLASSIFIED BY THE AGE OF THE ROCKS.<sup>1</sup>TABLE 16.—*Igneous rocks.*

Order.	Age.	No. of analyses.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
1	Archean .....	7	0.03	7.44	0.35	0.07	3.79	0.21	11.89
2	Proterozoic .....	8	.00	1.85	.31	.07	2.08	.16	4.47
3	Tertiary .....	18	.00	1.20	.13	.05	.53	.07	1.98
4	Recent lavas .....	5	.03	.41	.07	.01	.06	.02	.60
	Total Pre-Cambrian .....	28	.02	2.76	.23	.06	2.12	.12	5.31
	Grand total .....	51	.01	2.16	.18	.05	1.36	.09	3.85

In addition to those rocks which could be classed either as Archean or Proterozoic, there were others which could only be called Pre-Cambrian; they are included under the head of Total Pre-Cambrian.

The rapid and steady decline in the quantity of every gas, in passing down the columns from the Archean through the Proterozoic and Tertiary to Recent lavas, is very striking. These differences may be due to a combination of causes. The older rocks may yield more gas than the recent, owing to metasomatic changes which have been slowly taking place within the rocks. If this be so, the analyses indicate that this process is progressing at an exceedingly slow rate. Or the early magmas may have been more highly charged with gas, some of which has escaped as they were worked over and over and brought to the surface in later times. Both of these processes have probably been operative.

TABLE 17.—*Sedimentary and meta-sedimentary rocks.*

Order.	Age of rocks.	No. of analyses.	H <sub>2</sub> S, SO <sub>2</sub> .	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
1	Proterozoic .....	17	0.45	0.68	0.17	0.04	1.32	0.05	2.71
2	Paleozoic .....	10	.00	1.34	.25	.05	.41	.13	2.28
3	Mesozoic .....	1	.00	carb.	.15	.04	.45	.04	.68
	Total .....	28	.27	.93	.20	.04	.96	.08	2.48

<sup>1</sup> In this classification of analyses by the age of the rocks, and in the following one based on granularity, only my own analyses have been used.



Age appears to make less difference in the gas evolved from sedimentary or meta-sedimentary rocks than it does in the case of igneous rocks. All of the Proterozoic specimens were of metamorphic types, while only one of the Paleozoic sediments had been metamorphosed. The Mesozoic representative was a Jurassic shale altered by an intrusive. The unusual amount of sulphur gas in the Proterozoic list is due to two weathered rocks which contained iron sulphate. However, even with these omitted, the hydrogen sulphide is abnormally high in the rocks of this age. One of the Paleozoic shales was so calcareous as to yield 9.28 volumes of carbon dioxide, which accounts for the large quantity of this gas. The two bituminous shales (analyses 41 and 42) are not included in these averages, since their excessive volume of gas from organic sources would so influence the figures as to disguise some of the characteristics of the other rocks.

## ANALYSES CLASSIFIED BY THE GRANULARITY OF THE ROCKS.

TABLE 18.—*Igneous rocks.*

Order.	Granularity.	No. of analyses.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N <sub>2</sub> .	Total.
1	Fine-grained .....	22	0.02	2.75	0.31	0.06	1.68	0.12	4.94
2	Medium-grained .....	18	.01	2.37	.17	.05	1.41	.10	4.11
3	Coarse-grained .....	11	.01	.40	.10	.04	1.20	.08	1.83
4	Various porphyries (mostly Tertiary) .....	5	.00	.41	.07	.04	.22	.05	.79

From this table it would appear that the fine-grained rocks give off more gas than those of coarser granularity. One of the reasons for this difference probably lies in the fact that metasomatic changes are favored in fine-grained rocks, whose crystals, being smaller, afford more numerous junction-planes between the crystals, through which solutions more readily traverse the rock than in the coarse-grained varieties. Among other changes, hydration and carbonation should alter fine-grained rocks more effectively than coarse-grained ones.

Fineness of grain in igneous rocks usually means that the lava cooled rapidly, and this would hinder the escape of the inclosed gas. But in the process of slow crystallization, such as produces large crystals and coarse texture, much more of the gas would be likely to be crowded out of the growing crystals. However, as a general rule, fine-grained igneous rocks are surface flows, while coarse-texture types were formed at some depth below the surface, and hence a larger proportion of whatever gas was expelled from the rapidly cooling lavas would be more likely to escape altogether than would be the case with the gas which was excluded from growing crystals in deeper horizons, as in bathylithic intrusions, where final escape was difficult. In this problem of granularity, as in the matter of age, the quantities of gas evolved are probably determined by a combination of complex factors rather than by any single cause.

## RESULTS AT DIFFERENT TEMPERATURES.

The different gases are not all expelled from rock material at the same temperature, nor are they evolved at the same rate. In general, hydrogen sulphide and carbon dioxide are not only the first gases to appear, but

they are more rapidly given off than the others. Carbon monoxide follows the dioxide as the temperature is raised, and generally increases in relative importance, as the latter begins to subside, toward the end of the combustion. Hydrogen and marsh-gas are most conspicuous at high temperatures, and hence attain higher percentages in the last half of the gas than in the first portion. Nitrogen appears to be disengaged with much difficulty, requiring considerable time at an elevated temperature. These general facts may be graphically represented by plotting the curves based on the experiments with the Baltimore gneiss.<sup>1</sup> (See fig. 1.)

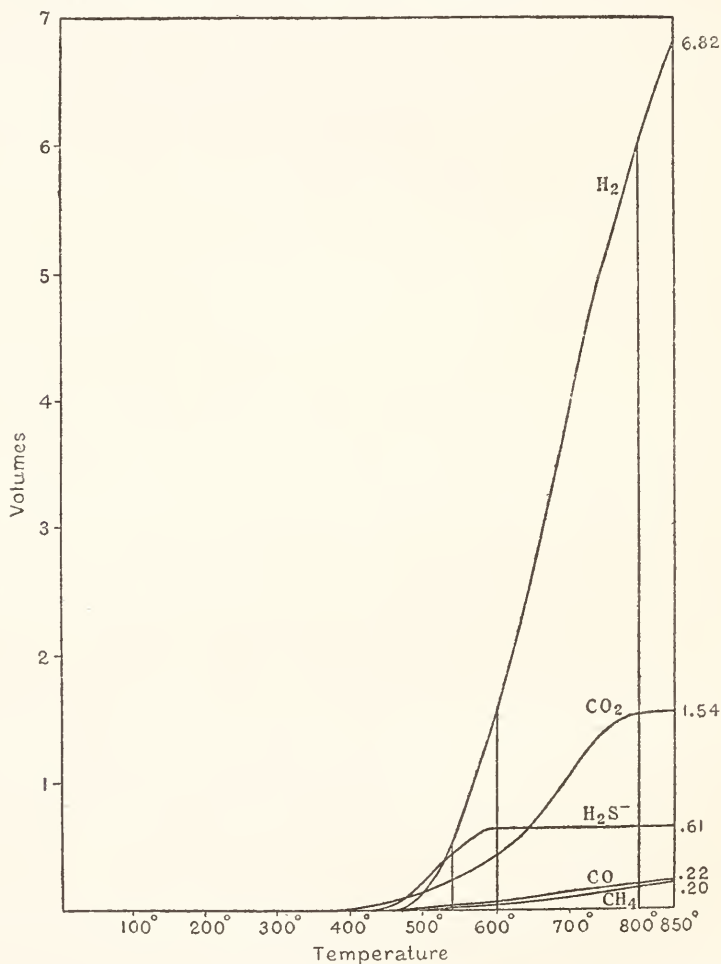


FIG. 1.—Plot of curves representing volume of each gas per volume of rock obtained at different temperatures from Baltimore gneiss.

Nitrogen is omitted from this diagram owing to an unfortunate leakage of air during a part of the experiment, which was sufficient to vitiate the results for this gas.

<sup>1</sup> For tables, see pp. 36-37.

## ABSORPTION.

To determine how much gas might be reabsorbed after being expelled by heat, it was thought desirable to use a rock capable of producing a large volume of gas. For this purpose a diabase from Nahant, Massachusetts, which yielded 13.9 volumes of gas, was selected. This material was heated at full blast until the gas evolution had practically ceased, which required about four hours; 182 cubic centimeters of gas were obtained. After allowing the powder to remain in the vacuum overnight, it was removed and still more finely pulverized in an agate mortar. It was then submitted to forced heat, yielding an additional 20 cubic centimeters of gas in six hours. On the third day the powder gave up but 1 cubic centimeter in four hours. As practically all the gas available under these conditions was now removed, the heat was turned off, and 132.01 cubic centimeters of this gas (at 27.0° and 758 millimeters) immediately introduced into the combustion-tube, which was allowed to cool. At the end of 43 hours 101.84 cubic centimeters (at 20.0° and 750 millimeters) remained to be pumped out. This being equivalent to 103.73 cubic centimeters at 27.0° and 758 millimeters, leaves 28.28 cubic centimeters as the volume of gas absorbed by the powder. The material in the tube was now heated for 2½ hours, but only 3.47 cubic centimeters could be extracted before the gas evolution ceased. Of this, carbon dioxide constituted more than 85 per cent. There still remain 24.81 cubic centimeters lost in the operation—a loss which is probably to be attributed to the oxidation of that quantity of hydrogen to water by ferric oxide, while the tube was cooling. This water-vapor being removed by the calcium chloride drying-tube, hydrogen could not be again freed by the reverse reaction when the tube was reheated. The carbon dioxide may be explained by carbonation of iron or calcium and the subsequent decomposition of these carbonates when heated the second time.

In order to ascertain how much absorption there might be at ordinary temperatures, 72 cubic centimeters of the remaining gas, from which the carbon dioxide had been removed, since carbonation is a recognized process, was allowed to stand in the tubes for eight days. At the end of this time no appreciable quantity of the gas had been absorbed. From this and the preceding experiment, it is quite evident that while rock material may take up certain gases while cooling from a higher temperature under special conditions, at ordinary temperatures absorption, if it goes on at all, takes place very slowly. Reversible chemical reactions undoubtedly play an important part in such absorption as takes place under changing temperatures.

Professor Dewar experimented with celestial graphite to ascertain its absorbing power for certain gases. After exhausting the graphite of its gases, dry carbon dioxide was drawn through the tube for twelve hours at ordinary temperatures. The tube was then heated and about 1.1 volumes of gas, containing 98.4 per cent carbon dioxide, pumped off. The graphite on the first heating had given 7.25 volumes of gas, of which 91.8 per cent was carbon dioxide. Dry marsh-gas was next passed over the

powder for twelve hours; upon heating, only 0.9 volume, containing 94.1 per cent carbonic acid, was obtained. The same experiment repeated with hydrogen gave only 0.17 volume, in which carbon dioxide reached 95 per cent.<sup>1</sup> From these figures it would seem that absorption is not very important. The steadily decreasing volumes of gas with each successive heating show the difficulty with which the gas is expelled, for apparently it is liberated more readily after an interval of time than if reheated immediately. Hence, unless the material used be completely deprived of its gas, there is always a danger in assigning to absorption what may, in reality, be only the last portions of the original gas.

Wright used another method in testing the hypothesis that the gas obtained from meteorites has been derived from our atmosphere by a process of absorption. He believed that if the gas be due to absorption from the earth's atmosphere, a meteorite should have stored up more of it after being exposed for a considerable period than shortly after its fall. His original analysis of the gas from a meteorite which fell in Iowa County, Iowa, on February 12, 1875, was made a short time after its fall. A year later, to extract the same quantity of gas from another fragment of the same meteorite required not only a longer time than in the first analysis, but more intense heating as well.<sup>2</sup> If any difference actually existed, a loss rather than a gain was indicated in this interval.

To test the effect of air exposure on a rock powder which had previously been heated until the gas evolution had completely ceased, the exhausted powders of my investigation were kept stored in paper bags, and several of them were reheated after intervals of some months. Two analyses of the iron basalt from Ovifak, Greenland, made 10 months apart, were as follows:

TABLE 19.

	Analysis No. 45.	Analysis after 10 months.
Hydrogen sulphide .....	0.00	0.00
Carbon dioxide .....	3.74	1.18
Carbon monoxide .....	1.74	.30
Methane .....	.17	.03
Hydrogen .....	2.24	.04
Nitrogen .....	.16	.21
Total .....	8.05 vols.	1.76 vols.

This basalt yielded about one-third as much carbon dioxide after the interval as it did when originally heated, but the hydrogen in the second portion of gas was almost a negligible quantity.

A second test was made with a chloritoid schist from the Black Hills, after an interval of more than a year.

<sup>1</sup> Sir James Dewar, Proc. Roy. Inst., vol. 11 (1886), p. 547.

<sup>2</sup> Wright, A. W., Am. Jour. Sci., vol. 11 (1876), p. 262.

TABLE 20.

	Analysis No. 23.	Analysis a year later.
Hydrogen sulphide .....	0.00	0.00
Carbon dioxide .....	.46	.29
Carbon monoxide.....	.10	.21
Methane .....	.04	.08
Hydrogen .....	3.07	2.11
Nitrogen .....	.05	....
Total .....	3.72 vols.	2.69 vols.

In this case, hydrogen has been restored somewhat more completely than carbon dioxide. Both of them amount to approximately two-thirds of the original volume of these gases.

A third test was made with amphibolite, after an interval of four months.

TABLE 21.

	Analysis No. 94.	Analysis four months later.
Hydrogen sulphide .....	0.00	0.00
Carbon dioxide .....	2.23	.64
Carbon monoxide.....	1.10	.34
Methane .....	.10	.12
Hydrogen .....	2.84	1.86
Nitrogen .....	.13	.09
Total .....	6.40 vols.	3.05 vols.

The recovery is here more marked in the case of hydrogen than in that of carbon dioxide.

A fourth test was made with Keweenaw diabase from Houghton, Michigan, after an interval of six months.

TABLE 22.

	Analysis No. 85.	Analysis 6 months later.
Hydrogen sulphide .....	0.00	0.00
Carbon dioxide .....	1.31	1.33
Carbon monoxide.....	.09	.08
Methane .....	.09	.03
Hydrogen .....	2.34	.43
Nitrogen .....	.05	.05
Total .....	3.88 vols.	1.92 vols.

After reposing six months in a paper bag, this diabase gave as much carbon dioxide, when heated, as it had in the first combustion; but less than one-fifth as much hydrogen was evolved on the second heating.

It is clear that an interval of time partially restores the gas-producing properties of these rock powders. For this phenomenon, there are two possible explanations. Either the first heating does not expel all of the gas contained in the rock, which, by some sort of diffusion or molecular



rearrangement, gradually prepares itself to come off when again heated, or else the rock powder absorbs gases from the atmosphere. If the carbon dioxide were derived from the decomposition, at high temperatures, of a carbonate such as that of calcium, the oxide of calcium thus produced would be likely to capture carbon dioxide from the air, though perhaps this would be a slow process in a paper bag where the circulation of air was comparatively limited. Also, if the hydrogen came from chemical reactions between ferrous salts and water combined in hydrated minerals, the atmosphere might have restored to these minerals some of the water which they lost when first heated. It was thought that rehydration, if combined water be a vital factor in the production of hydrogen, could be more readily effected by placing the exhausted powder in water for a few days than by wrapping it up in a paper bag for as many months.

Accordingly, the Keweenaw diabase powder (No. 85) which originally gave 3.88 volumes, and after six months 1.92 volumes, was heated a third time (a week later) with the evolution of very little gas. This powder, after cooling in the vacuum, was taken out of the combustion-tube and immediately placed in a flask filled with freshly distilled water. A stopper being fitted into the flask, it was allowed to stand for 66 hours. At the end of this time, the water was poured off, the powder quickly, but thoroughly, dried and put into the combustion-tube. When heated, this powder gave off 0.79 volume of gas; but instead of being largely hydrogen, 67.72 per cent of this was carbon dioxide. Hydrogen amounted to only 14.69 per cent, while carbon monoxide reached 15.06 per cent. An analysis of this gas gave:

TABLE 23.

	Percentages.	Volumes.
Carbon dioxide .....	67.72	0.53
Carbon monoxide .....	15.06	.12
Methane .....	.19	.00
Hydrogen .....	14.69	.12
Nitrogen .....	2.34	.02
Total .....	100.00	.79

This carbon dioxide could not have come from the air, but must have existed within the material and must have withstood three successive heatings in the combustion-tube. From a comparison of these figures with the two previous analyses of the gas from this material, what is true of the carbon dioxide would appear to be true of the hydrogen as well. This experiment favors the conclusion, that the gas which is obtained from a rock powder by a second heating after a period of time, is not due to a process of selective absorption from the atmosphere, but rather to changes which have been slowly taking place within the powder itself.

However, the results of these experiments upon the absorption of gas by rock powders at ordinary temperatures and pressures can not throw much light upon the source of the gases, or how they came to be embodied in the rocks, since the conditions under which the rocks were formed must have been very different. While high temperatures, in general, tend to

expel the gaseous constituents of the rocks, high pressures would have the effect of promoting absorption. Moreover, it is possible that molten lavas might absorb, or dissolve, certain gases without an increase of pressure. But the testimony of volcanic gases and of the scoriaceous surfaces of lava flows favors the idea that gases and vapors are constantly being boiled out of molten lavas whenever exposed under the ordinary atmospheric pressure. Lavas give off gas rather than absorb it, at the earth's surface; however, at considerable depths below the surface the action may be entirely different. If the conception be entertained that the earth's interior is, for the most part, solid with only threads of liquid lava here and there, the question for this solid portion would be one of the ability of great pressure to cause a solid to absorb gases. This need not be further dwelt upon, since most of the igneous rocks which are accessible have been in the liquid state at some time. In the case of the threads of liquid magma there is reason to suppose that gas, if it could be brought into contact with this lava, would become incorporated in it owing to the great pressure. But this does not explain the original source of the gases, nor how they can be brought in contact with the liquid rock under the prevailing conditions of temperature and pressure.

### STATES IN WHICH THE GASES EXIST IN ROCKS.

In order to explain the immediate source of the gases obtained by heating rock material in vacuo, three different hypotheses naturally present themselves. The simplest of these is to suppose the gases to exist in minute cavities or pores, having been entrapped within the rock during the process of solidification. This supposition is suggested and supported by the observation that microscopic slides of some minerals, notably quartz and topaz, reveal numerous small gas-bubbles. But while there is evidence that some gas is thus held in cavities, there is equally strong evidence to show that the greater part of it can not be attributed to this source.

To escape the difficulties encountered by the first hypothesis, appeal is made to the imperfectly understood property of some of the elements to "occlude," or dissolve within their mass, certain gases. It is remembered that under the proper conditions palladium will occlude 900 times its own volume of hydrogen, and that the same gas is also absorbed, in lesser degree, by other metals, particularly platinum and iron, while silver has a similar affinity for oxygen. This principle applied to igneous rocks as a hypothetical source of their gases becomes at once a more difficult proposition to prove or disprove.

The third hypothesis, more conservative than either of the others, assumes that these gases do not exist in the rocks in the uncombined, or gaseous state, but are produced in the combustion-tube by chemical reactions at high temperature. The oxides of carbon and sulphur are assigned to the decomposition of carbonates and sulphates; methane to organic matter present, carbides, or to high temperature reactions between hydrogen and the carbon gases; sulphureted hydrogen to sulphides; nitrogen to nitrides; while hydrogen is liberated from steam by the action of metallic iron or ferrous salt.

## GASES IN CAVITIES.

The studies of Brewster, Davy, Sorby, Hartley, and others, have established the presence of gas, generally carbon dioxide, though sometimes nitrogen, in the minute cavities of certain crystals. This has been widely known to geologists, and hence, when it was discovered that many crystalline rocks yield gas upon heating in vacuo, it was natural to suppose that the gas came from cavities. Such was the view taken by Tilden.<sup>1</sup> But while microscopical investigations indicated that carbon dioxide constitutes more than 90 per cent of the gaseous matter inclosed in these cavities, and hydrogen is not found in more than traces, the latter gas is the most important constituent of the mixture derived from rocks by heat. In addition to this, the observation that those rocks which are not known to contain many gas cavities produced several times as much gas as the cavernous quartzes also suggested that the bulk of the gas, at least, could not be attributed to inclosure in cavities. Moreover, basic rocks were found to be more productive than acidic, whereas it had generally been supposed that the latter, owing to their greater viscosity, should entrap more gas and vapor than the more fluid basic lavas.

The suspicion that the gas did not come from cavities in any large degree was strengthened by the observation that the composition of the gas varied according to the temperature to which the rock powder was heated. If the gas comes from cavities, its liberation should commence with a slight rise of temperature and should continue more or less steadily, as the heat increases, until the expansive force of the gas opens up most of the pores. Since all gases expand equally, one should burst its confines as soon as another, and a sample of gas obtained at any given temperature should not differ very widely in composition from that evolved at any other.

Neglecting hydrogen sulphide and nitrogen, the character of the gas obtained at various temperatures from Baltimore gneiss<sup>2</sup> is shown by the following table:

TABLE 24.

Gas.	At 360°.	At 448°.	At 540°.	At 600°.	At 800°.	At 850°.
Carbon dioxide .....	93.7	37.5	27.0	13.6	19.3	0.0
Carbon monoxide.....	6.3	4.2	2.4	2.3	2.8	1.1
Methane .....	0.0	25.0	1.8	2.5	2.1	3.4
Hydrogen .....	0.0	33.3	68.8	81.6	75.8	95.5
Total.....	100.00	100.00	100.00	100.00	100.00	100.00
Volumes .....	.03	.03	1.28	1.40	5.30	.94

Or, combining the separate analyses so that each figure represents the percentage of the total gas obtained up to the specified temperature, the result is as shown in table 25:

<sup>1</sup> Tilden, Chem. News, vol. 75 (1897), p. 169; Proc. Roy. Soc., vol. 64 (1897), p. 453.

<sup>2</sup> Material of analysis, No. 28.



TABLE 25.

Gas.	20° to 360°	20° to 448°	20° to 540°	20° to 600°	20° to 800°	20° to 850°
Carbon dioxide .....	93.7	69.7	30.1	20.2	19.5	17.5
Carbon monoxide.....	6.3	5.3	2.5	2.4	2.7	2.6
Methane .....	0.0	10.7	2.4	2.5	2.2	2.3
Hydrogen .....	0.0	14.3	65.0	74.9	75.6	77.6
Total.....	100.00	100.00	100.00	100.00	100.00	100.00
Volumes .....	.03	.06	1.34	2.74	8.04	8.98

Carbon dioxide thus appeared first, constituting 93 per cent of the gas evolved at 360° C., while hydrogen was not present in a measurable quantity. On the other hand, at the highest temperature used (850°) hydrogen amounted to 95 per cent of the total and carbon dioxide was entirely wanting. The steady decrease in the proportion of carbon dioxide with the elevation of the temperature, and the proportionate increase in the value of the hydrogen, are striking. The minor constituents, carbon monoxide and methane, underwent some variations, but did not change so radically. The former came off at the lower temperature, but declined at full red heat. Nitrogen, it appears from other experiments, does not appear in the gases obtained by moderate heating, but increases steadily in importance when the heat is carried higher. It is the last gas to be liberated.

The complete table, expressing the volumes of each gas per unit volume of gneiss, follows:

TABLE 26.

Temperature.	H <sub>2</sub> S.	CO <sub>2</sub> .	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	Total.
100°, boiling water .....	0.00	0.00	0.00	0.00	0.00	0.00
218°, boiling naphthalene.....	.00	.00	.00	.00	.00	.00
360°, boiling anthracene.....	trace	.03	tr.	.00	.00	.03
448°, boiling sulphur .....	trace	.01	tr.	.01	.01	.03
540°, metal bath .....	.42	.21	.02	.02	.54	1.28
600°, dull red heat .....	.18	.17	.03	.03	1.02	1.40
800°, full blast .....	.01	1.12	.16	.12	4.39	5.30
850°, forced heat .....	.00	.00	.01	.03	.86	.94
Total.....	.61	1.54	.22	.20	6.82	8.98

These results are graphically represented in the curves of figure 1.

The fact that little gas could be obtained below 450° is in itself a strong argument against the hypothesis that the gases come from pores, and there also seems no way in which the behavior of the gases, as set forth by these curves, can be consistently fitted into that theory.

#### TESTIMONY OF THE METEORITES.

Meteorites have already been subjected to investigation of this sort, though not with this purpose in mind. Mallet divided the gas which he extracted from the meteoric iron of Augusta County, Virginia, into three portions;<sup>1</sup> his results have been reduced by Wright<sup>2</sup> to the figures given in table 27:

<sup>1</sup> Mallet, Proc. Roy. Soc., vol. 20, p. 367.

<sup>2</sup> Wright, Am. Jour. Sci., vol. 2, p. 261.

TABLE 27.

	CO <sub>2</sub> .	CO.	H <sub>2</sub> .	N <sub>2</sub> .
Beginning .....	15.09	30.74	42.52	11.65
Middle .....	4.23	46.12	43.64	6.01
End .....	3.69	47.00	13.36	35.95

The analyses of meteorites by Wright show that, in all cases, carbon dioxide reached a higher percentage in the gas evolved at 500° than it did in that obtained at red heat, and that the reverse of this was true of hydrogen in the stony meteorites. In the iron meteorites, however, two analyses indicated a marked fall in hydrogen with the increase of heat, while the other two were characterized by an increase. Wright's figures for the meteorite from Guernsey County, Ohio, illustrate the continuous decrease in the percentage of carbon dioxide: At 100°, 95.92 p. ct.; at 250°, 86.36 p. ct.; at 500°, 82.28 p. ct.; incipient red heat, 33.55 p. ct.; red heat, 19.16 p. ct.

The volume of gas obtained at each temperature is only stated for 500° and red heat. These show that up to 500°, 2.06 volumes were evolved, and that above this point only 0.93 volume was received. From this it appears that the diminishing percentages of carbon dioxide above 500° represent an absolute slackening of the output of that gas, as well as an apparent decrease due to the greater evolution of hydrogen. It might be argued that in this case, where gas was produced at only 100°, the cavities contributed the carbon dioxide, yielding it early and then slackening, as would be expected; but even if this be admitted, the hydrogen manifestly can not be ascribed to that source. Tending in a measure to support this view is the work of Sorby,<sup>1</sup> who has shown that olivine crystals in the meteorites of Aussen and Parnallee, when examined under the microscope, contain numerous small cavities filled with gas, similar to those which have been observed in many terrestrial minerals.

In his earlier paper, Wright expressed the opinion that the gases were partly condensed upon the particles of iron and partly absorbed within them. Later he took the position that while some gas may be condensed upon the fine particles of iron, a large part of the carbon dioxide, and probably also of the other gases, is mechanically imprisoned in the substance of the meteorite. This view, which does not seem to be in accord with his researches at different temperatures, he bases largely upon a single experiment. Material from the Iowa meteorite was finely pulverized and the iron grains separated from the non-metallic powder. A third portion consisted of coarse fragments of the meteorite. The three portions heated for the same time gave the following results:

TABLE 28.

	CO <sub>2</sub> + CO.	H <sub>2</sub> .	N <sub>2</sub> .	Volumes.
Powder .....	66.96	30.96	2.08	0.97
Iron .....	38.72	59.38	1.90	0.51
Fragments .....	48.07	50.93	1.00	1.87

<sup>1</sup> Sorby, Proc. Roy. Soc., vol. 13 (1864), pp. 333-334.

The greater volume of gas from the fragments was taken to indicate that a portion of the gas was lost in the process of pulverization. An analysis of these figures reveals the fact that the difference in volume was chiefly due to the deficiency of the combined portions in hydrogen, instead of carbon dioxide, and that while there was also a slight loss of the latter gas, there was a decided gain in nitrogen.

Returning to the rocks, Tilden<sup>1</sup> is authority for the statement that it does not make much difference in the quantity of gas evolved, whether the material be taken in chunks or in a fine powder. Instead of abandoning the idea of cavities, he believed them to be very minute. But this is approaching an alternative hypothesis; if the reduction of the cavities is carried far enough—to intermolecular spaces—practical occlusion is the result.

Another objection to the theory of mechanically-retained gases apparently exists in the slowness with which the gas is liberated when the material is heated. Usually about three hours and often a very much longer time is required to expel the gas. Unless the gas from cavities be assumed to escape by diffusion through the walls of the inclosing mineral, instead of violently bursting its confines, there is no reason why it should not come off with a rush when the combustion-tube is heated rapidly to redness. Some rocks, generally those yielding a moderate quantity of gas in which carbon dioxide is the principal constituent, often give up their gas quickly—mostly within the first 60 to 90 minutes, although the generation continues for a longer time, before ceasing altogether. But other varieties of rock, particularly those noted for greater volumes, in which the percentage of hydrogen runs high, emit gas slowly and steadily for three or four hours.

These considerations led me to try a series of experiments which should show how much gas actually could be obtained from the opening of cavities alone. For this purpose a crusher was devised (fig. 2), capable of pulverizing a rock specimen in a complete vacuum. Adopting the principle of the familiar steel mortar, this was constructed in three pieces. The cylindrical cup in which the rock material is crushed possesses an internal diameter of 7 centimeters and a depth of 9 centimeters. The walls are purposely made thick and strong and the bottom is protected from the abrasion of hard minerals by inserting a disk of hardened steel. Inserted in the walls is a stopcock through which the apparatus is to be exhausted and the gases later pumped out. A circular steel cap, or cover, provided with six screws, whose sockets are depressed in the top of the cylinder, is intended to make the chamber of the mortar air-tight. In the center of the cap-

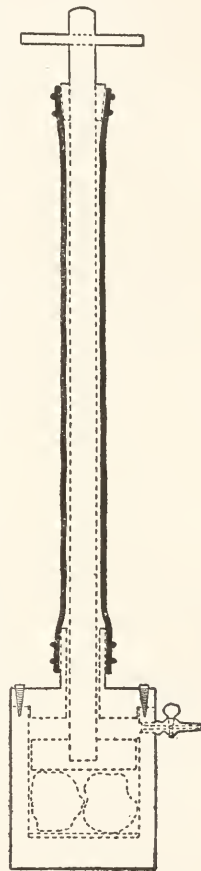


FIG. 2.—Apparatus for crushing rock specimens in vacuo.

<sup>1</sup> Tilden, Chem. News, vol. 75 (1897), p. 169; Proc. Roy. Soc., vol. 64 (1897), p. 453.

piece is a hole large enough to permit the ready movement of the piston-shaft. Around this hole on the upper side there is welded a short piece of steel tubing which is to guide the piston-rod and serve as a place of attachment for the rubber tubing in which the shaft of the piston is incased. The piston is a shaft 50 centimeters in length, 2.2 centimeters in thickness, to which is attached a head piece of hardened steel which will fit snugly into the cylinder. Near the upper end of the piston is a cross-bar serving as a handle, and also a flange to which the rubber tube is to be fitted.

When ready to put together, the piston-shaft is incased in a 1-inch tube of pure rubber, 45 centimeters long, which is tightly fitted and wired to the flange near the end of the rod, whereupon the other end of the shaft is slipped through the hole in the cover-piece, and the piston-head affixed. The lower end of the rubber tube is wired to the steel tube of the cover-piece which, after the rock specimen has been placed in the cylinder, is fitted with a rubber washer and screwed as tightly as possible to the cylinder. The rubber tube is taken of length sufficient to allow the head of the piston to touch the bottom of the cylinder; by pulling upward on the handle the rubber wrinkles and folds upon itself, affording ample play to the piston.

The stopcock is connected with the mercury-pump and the cylinder of the crusher exhausted, after which vigorous strokes delivered at the end of the piston with a heavy mallet crush the rock, thus opening the gas cavities. Whatever gas is liberated, is pumped into the receiver and analyzed in the ordinary way.

#### RESULTS.

Of the first rock tested, a basalt from the Faroë Islands, 42 grams were crushed finely enough to pass through a 30-mesh sieve, besides several times as much, less completely pulverized. In all, less than 0.1 cubic centimeter of gas was obtained, which may be considered as practically no gas at all, since this small quantity is within the leaking possibilities of the apparatus.

A slightly scoriaceous basalt from Hawaii produced about 0.1 cubic centimeter of gas, which appeared to be largely air. No carbon dioxide could be detected. Of this basalt, 18.3 grams passed through the sieve.

15.73 grams of vein quartz from Utah (No. 71 of the analyses) gave no trace of gas.

In an effort to demonstrate conclusively that the lack of gas liberated by crushing these lavas was not due to defective apparatus, a glass bulb of measured capacity, filled with air, was broken in the crusher in place of the rock ordinarily used. The result showed that gas introduced into the crusher can be extracted without sensible change in volume. As diffusion through the rubber tubing was considered a possible, though not very probable, source of error, a further trial was made, using hydrogen, lightest and most active among the gases, in order to put the apparatus to as severe a test as possible. The purity of this hydrogen had previously been established by analysis. The bulb broken, the gas was pumped off and exploded with air. The observed shrinkage agreed, within the limit of error, with the amount of hydrogen calculated to have been contained within the bulb.



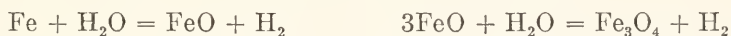
Being desirous of finding some specimen which would yield gas when crushed in this manner, I procured some crystals of cavernous quartz from Porretta, Italy, in which several of the cavities exceeded a millimeter in diameter. 5.91 grams were crushed to sufficient fineness to pass through the sieve, and 61.66 grams were partially crushed. 0.08 cubic centimeter of carbon dioxide was obtained, which, supposing that it all came from the 5.91 grams, would be equivalent to only 0.03 of the volume of the quartz. An analysis showed also a little methane and some nitrogen, but the amount of gas available was too small for the determination to be of any value.

The result of this last test agrees with the microscopic studies of the early investigators. Carbon dioxide exists in the cavities of quartz, but its volume, compared with the volume of the inclosing mineral, is small. Microscopical observations seem to show that gas cavities occur almost exclusively in a certain set of minerals which combine hardness usually with imperfect cleavage, namely, quartz, topaz, garnet, spinel, beryl, chrysoberyl, corundum in the form of rubies, sapphires, and emeralds, and diamond. These are minerals which, once they had inclosed gas, would hold it, even under great pressure.

## GASES DUE TO CHEMICAL REACTIONS.

### HYDROGEN.

The double series of iron salts, ferrous and ferric, together with the intermediate ferroso-ferric compounds, reacting with oxidizing or reducing agents, undergo various reversible reactions whose possibilities are great. When steam is passed over metallic iron or ferrous oxide at a red heat, it is decomposed, giving up oxygen to the iron, and at the same time producing free hydrogen. The reactions may be written:



Hydrogen is produced in this way most rapidly at temperatures about 500°. Stromeier is authority for the statement that the breaking up of water begins at 150° but takes place very slowly; at 200° somewhat more rapidly; at 360° the process requires several hours; at 860° it is complete in less than one hour; while near the melting-point of iron several minutes are sufficient.<sup>1</sup>

The authorities agree that ferric oxide is not formed in this process; the magnetic oxide,  $\text{Fe}_3\text{O}_4$  is the final product of the action of a current of steam upon ferrous oxide.<sup>2</sup>

But these reactions are completely reversible. According to Gay-Lussac, magnetite is reduced to the metal by hydrogen at every temperature between 400° and the highest degree of heat obtainable in the combustion-furnace, particularly at the same temperature at which steam is split up by glowing iron.<sup>3</sup> Siewert states that ferric oxide (from the oxalate) is not altered by hydrogen at 270° to 280°; between 280° and 300°

<sup>1</sup> Stromeier, Pogg. Ann., vol. 9, p. 475.

<sup>2</sup> Among others, Regnault, Ann. de Chim. et Phys., vol. 62, p. 346.

<sup>3</sup> Gay-Lussac, Ann. de Chim. et Phys., vol. 1, p. 33.



it is reduced to ferrous oxide, and when heated above  $300^{\circ}$ , to the metal.<sup>1</sup> The more recent studies of Moissan give different figures;<sup>2</sup>  $\text{Fe}_2\text{O}_3$  is reduced by hydrogen at  $300^{\circ}$  to  $\text{Fe}_3\text{O}_4$  in 30 minutes; at  $500^{\circ}$  to  $\text{FeO}$  in 20 minutes; at  $600^{\circ}$  to  $700^{\circ}$  to metallic iron.

If the hydrogen or water-vapor produced by these reactions is not removed, the process continues only until a condition of equilibrium is established. In extracting the gases from rocks, the products of these reactions were rapidly removed, so that final equilibrium was probably never attained. Hence, in these experiments the direction in which the reaction will proceed depends upon whether there is ferrous oxide and water, or ferric oxide and hydrogen, most abundantly stored in the rock. Ferrous and ferric salts behave, in general, like the oxides.

Since most igneous rocks contain ferrous as well as ferric salts, the possibility that, when heated in the presence of steam, hydrogen will be produced, must always be taken into account. In terrestrial rocks water of constitution is generally present and often is not expelled below a bright red heat. Thus, a rock containing a ferrous compound in appreciable amount, together with water of crystallization, a portion of which is retained up to red heat, will be in a condition to furnish hydrogen upon the application of heat.

In general, the analyses show that the greater the amount of iron present in the rock, the more hydrogen may be expected. This may be the result of chemical action, or a selective occlusion of hydrogen manifested by iron and its compounds. Magnetite, being the end product of the reaction of water upon iron, can not produce hydrogen by this chemical interaction, though it might possess the occlusive properties of iron compounds. Analysis of the black sand from the bed of the Snake River, Idaho,<sup>3</sup> indicates that iron in the form of magnetite does not yield much hydrogen. However, these figures have no great significance, for, even though an abundance of hydrogen existed in the ore, either occluded or mechanically imprisoned, the magnetite would, at red heat, quickly oxidize it to water, with the exception of a small portion of free hydrogen maintained by the reverse reaction. The analyses show that basic diabases and basalts yield the most gas, while acidic rhyolites give but little. These are also among the maximum and minimum iron-bearing lavas. But the difference in hydrogen is much greater proportionately than the difference in ferrous salts. Table 13<sup>4</sup> also shows that andesites, which are nearer the basic end of the scale than the acidic, do not greatly exceed the rhyolites in hydrogen. The difference between the two types of rocks, acidic and basic, in point of volume of the individual gases, while somewhat more conspicuous in the case of hydrogen, is generally true of the other gases as well.

Endeavoring to prove that the hydrogen obtained by heating minerals came entirely from chemical reactions, Travers experimented with the secondary mineral chlorite, calculating how much ferrous iron should have been oxidized to give the quantity of hydrogen and carbon monoxide evolved.<sup>5</sup> This he found to agree closely with the difference in amount of

<sup>1</sup> Siewert, Jahresbericht d. Chem., 1864, p. 265.

<sup>4</sup> Ante, p. 27.

<sup>2</sup> Moissan, Comptes Rendus, vol. 84, p. 1296.

<sup>5</sup> Travers, Proc. Roy. Soc., vol. 64, p. 132.

<sup>3</sup> Analysis No. 46.

ferrous iron present before and after heating. Another test with feldspar from the Peterhead granite not showing correspondence, seemed to Travers to be explained by the presence of both metallic iron and ferrous oxide in the feldspar. The presence of a considerable amount of metallic iron in a feldspar which crystallized from an acidic magma containing an excess of silica is quite unusual. This feldspar treated with dilute sulphuric acid yielded about four volumes of hydrogen.

Against the theory that the hydrogen was largely derived from the action of water-vapor on ferrous compounds, may be placed the very marked change in color which the rock undergoes during the process of heating. I have observed that whenever a rock powder, before being placed in the tube, possesses an orange, brownish, or reddish tint due to ferric oxide, the combustion invariably alters the tone to a greenish gray. This suggests a reduction of ferric oxide to ferrous oxide, a process consuming hydrogen. In order to test this question, a specimen of bright-red Permian sandstone from the Garden of the Gods near Colorado Springs<sup>1</sup> was powdered. These Red Beds are supposed to consist of thoroughly oxidized material; this opinion was partially confirmed by chemical tests which gave a weak reaction for ferrous iron, but indicated much ferric. After heating, the brick-red sand had become dull gray-green in color. The gray sand from the combustion-tube gave a stronger reaction for ferrous iron. Later, a quantitative determination of the ferrous iron present before and after heating was undertaken. Equal weights of the two sands were boiled with strong sulphuric acid<sup>2</sup> for two hours and then allowed to stand overnight. In each case the solution was effected in an atmosphere of carbon dioxide to prevent oxidation by oxygen from the air. The two solutions were then titrated with potassium permanganate solution. 3.09 grams red sand required 1.97 cubic centimeters N/10  $\text{KMnO}_4$ ; 3.09 grams gray sand required 2.52 cubic centimeters N/10  $\text{KMnO}_4$ . 0.55 cubic centimeter N/10  $\text{KMnO}_4$  is equivalent to 0.015 gram of iron, which is the weight of the metal reduced from the ferric to the ferrous state. For the total weight of sand used in the gas analysis (85 grams), the increase in ferrous iron should be 0.423 gram, which would correspond to an oxidation of approximately 85 cubic centimeters of hydrogen. Yet both hydrogen and carbon monoxide were obtained from this sandstone in considerable quantities.

TABLE 29.

	Per cent.	Volumes.
Hydrogen sulphide .....	0.05	0.00
Carbon dioxide .....	carbonated	
Carbon monoxide.....	60.69	.71
Methane .....	6.27	.07
Hydrogen .....	27.28	.32
Nitrogen .....	5.71	.06
Total .....	100.00	1.16

<sup>1</sup> Analysis No. 78.<sup>2</sup> 3 parts conc. acid to 1 part water.

In order to ascertain the quantitative effect of the presence of ferric oxide in moderate amount, 0.77 gram of pure  $\text{Fe}_2\text{O}_3$  was mixed with 20.04 grams of diabase powder, tinting this latter a reddish brown. An analysis of the resulting gas and of the original diabase gave the figures shown in the following table:

TABLE 30.

	Resulting gas.			Original diabase, <sup>1</sup>	
	Per cent.	Volumes.		Per cent.	Volumes.
Hydrogen sulphide .....	0.06	0.00	Hydrogen sulphide .....	0.04	0.00
Carbon dioxide .....	72.99	7.08	Carbon dioxide .....	61.25	8.51
Carbon monoxide .....	3.90	.38	Carbon monoxide .....	2.47	.34
Methane .....	.87	.09	Methane .....	1.32	.18
Hydrogen .....	20.79	2.01	Hydrogen .....	33.69	4.68
Nitrogen .....	1.39	.13	Nitrogen .....	1.23	.17
Total .....	100.00	9.69	Total .....	100.00	13.88

<sup>1</sup> Analysis No. 86.

A comparison of these results shows that, while the yield of hydrogen was diminished by the ferric oxide to less than half of what it would have been, the carbon monoxide was not affected. The ferric oxide apparently only went down to a state of equilibrium, and was not in sufficient quantity to offset the copious evolution of hydrogen from the diabase. The brown color, however, was replaced by green.

To get rid of the iron, and particularly ferrous iron, material from the same diabase specimen was treated with concentrated nitric acid for 66 hours. Much gas came off at first, nitric oxide, perhaps from the action of the acid on pyrite, being very conspicuous. The powder, washed repeatedly on a filter until all the acid had been removed, was dried in an oven overnight and then heated at  $115^\circ$  in an air-bath for half an hour. Two and a half hours at red heat, in vacuo, then expelled only 0.23 volume of gas from the diabase powder. Its composition is given in table 31.

TABLE 31.

	Per cent.	Volumes.
Hydrogen sulphide .....	0.00	0.00
Carbon dioxide .....	25.23	.06
Carbon monoxide .....	20.15	.05
Methane .....	6.36	.01
Hydrogen .....	21.21	.05
Nitrogen .....	27.05	.06
Total .....	100.00	.23

A similar test was made with dilute sulphuric acid, in a vacuum. In this experiment, the gas driven off by the acid during the first  $2\frac{1}{2}$  hours was collected and analyzed. Table 32 shows this to have been chiefly carbon dioxide.

TABLE 32.

	Per cent.	Volumes.
Hydrogen sulphide .....	0.00	0.00
Carbon dioxide .....	98.10	6.44
Carbon monoxide } .....	.03	.00
Methane .....		
Hydrogen .....	.25	.02
Nitrogen .....	1.62	.10
Total .....	100.00	6.56

As a precautionary measure, to avoid the introduction of any metallic iron in the process of pulverization, the diabase was reduced to a powder in an agate mortar. The brass sieve was not used. Hence this hydrogen did not come from any action of the acid upon a metal introduced during the manipulations.

This powder, after remaining in a vacuum with an excess of sulphuric acid for three days, was washed thoroughly on a Gooch filter until the last traces of calcium sulphate had been removed. After drying for an hour at 125°, the powder was placed in the combustion-tube and heated to redness. The sulphuric acid left more gas in the rock than the nitric.

TABLE 33.

	Per cent.	Volumes.
Hydrogen sulphide .....	13.30	0.21
Carbon dioxide .....	38.19	.62
Carbon monoxide .....	9.01	.14
Methane .....	3.95	.06
Hydrogen .....	33.80	.54
Nitrogen .....	1.75	.03
Total .....	100.00	1.60

From these experiments it would appear that acids remove the critical gas-producing factors without liberating a notable amount of any gas except carbon dioxide. Whether hydrogen may not pass into solution with the iron, without being freed, is a question which naturally arises, but the balance of chemical opinion is against this supposition.

Professor Dewar digested celestial graphite in strong nitric acid for several hours and, after washing and drying, found that with heat it gave exactly the same amount of hydrogen as before treating with the acid. This would suggest that, in the case of celestial graphite, the hydrogen was not connected with iron, but existed in some very stable form.<sup>1</sup>

If all the hydrogen was produced by the reaction of water on ferrous salts, it would seem as if the volume obtained should bear a direct relation to the quantity of these two critical constituents present in the rock. To throw light on this matter, two rocks of the same origin, but of different chemical composition, presented the most favorable line of attack. An intrusive andesite and a specimen of vein quartz derived from the mag-

<sup>1</sup> Dewar, Proc. Roy. Inst., vol. 11, p. 550.



matic waters of the intrusion, kindly furnished by Dr. C. K. Leith, were used to illustrate this point.<sup>1</sup> Though containing very different quantities of ferrous compounds, they yielded identical volumes of methane, hydrogen, and nitrogen. These analyses are given in table 34.

TABLE 34.

	Andesite.			Vein quartz.	
	Per cent.	Volumes.		Per cent.	Volumes.
Hydrogen sulphide.....	0.03	0.00	Hydrogen sulphide .....	0.00	0.00
Carbon dioxide .....	77.50	2.66	Carbon dioxide .....	13.93	.11
Carbon monoxide.....	4.75	.16	Carbon monoxide.....	11.26	.09
Methane .....	.95	.03	Methane .....	4.00	.03
Hydrogen .....	15.35	.53	Hydrogen .....	64.40	.53
Nitrogen .....	1.42	.05	Nitrogen .....	6.41	.05
Total .....	100.00	3.43	Total .....	100.00	.81

The great excess of carbon dioxide in the andesite is assigned to carbonation of that lava subsequent to its formation—a process to which the quartz would not be susceptible.

The observation that comparatively pure quartz yielded half a volume of hydrogen suggested a quantitative analysis to determine the amount of iron actually contained in hydrogen-producing quartz. For the purpose quartz from Orange, New South Wales, was selected. 102.72 grams of the quartz yielded 4.81 cubic centimeters of hydrogen at 0° and 760 millimeters.<sup>2</sup> After the gas had been extracted, two different portions of the exhausted mineral were digested with aqua regia—one of them boiled for an hour, the other being allowed to stand during several days, and occasionally warmed to the boiling-point. The acid may be considered to have dissolved all the iron from which gas could have escaped. To make the case certain, all of the iron detected has been supposed to have existed in the quartz as ferrous oxide, although some of it undoubtedly occurred in the form of ferric compounds. The iron was weighed as  $\text{Fe}_2\text{O}_3$ .

First determination:

22.22 gms. quartz contained.....	0.0015 gm. $\text{Fe}_2\text{O}_3$
102.72 gms. quartz would contain.....	.00693 gm. $\text{Fe}_2\text{O}_3$
102.72 gms. quartz would contain.....	.00485 gm. Fe
Fe (as FeO) required to give 1 c.c. hydrogen .....	.00748 gm.
Maximum amount hydrogen from reaction.....	.65 c.c.
Hydrogen actually obtained (at 0° and 760 mm.).....	4.81 c.c.
Hydrogen not from this reaction.....	4.16 c.c.

Second determination:

52.02 gms. quartz contained.....	0.0042 gm. $\text{Fe}_2\text{O}_3$
102.72 gms. quartz would contain.....	.00829 gm. $\text{Fe}_2\text{O}_3$
102.72 gms. quartz would contain.....	.00580 gm. Fe
Fe (as FeO) required to give 1 c.c. hydrogen .....	.00748 gm.
Maximum amount hydrogen from reaction.....	.77 c.c.
Amount of hydrogen actually obtained.....	4.81 c.c.
Hydrogen not from this reaction.....	4.04 c.c.

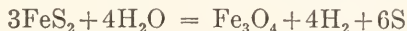
<sup>1</sup> Analyses Nos. 70 and 71.

<sup>2</sup> Analysis No. 100.



According to these two determinations, this quartz evolved respectively 7.4 or 6.2 times as much hydrogen as could have been generated by the reaction  $3\text{FeO} + \text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + \text{H}_2$ .

If the iron existed as pyrite, four times as much hydrogen as could come from ferrous oxide might have been produced in accordance with the equation



On the basis of this equation the excess of hydrogen from the quartz is much reduced.

First determination:

102.72 gms. quartz contain.....	0.00485 gm. Fe
Fe (as $\text{FeS}_2$ ) required to give 1 c.c. hydrogen .....	.00187 gm.
Hydrogen possible from reaction.....	2.60 c.c.
Hydrogen actually obtained.....	4.81 c.c.
Hydrogen not from this reaction.....	2.21 c.c.

Second determination:

102.72 gms. quartz contain.....	0.00580 gm. Fe
Fe (as $\text{FeS}_2$ ) required to give 1 c.c. hydrogen.....	.00187 gm.
Hydrogen possible from reaction.....	3.08 c.c.
Hydrogen actually obtained.....	4.81 c.c.
Hydrogen not from this reaction.....	1.73 c.c.

These computations assume not only that all the iron in the quartz was combined as pyrite, and that it was completely oxidized to magnetite, but that the hydrogen sulphide produced was entirely dissociated into hydrogen and sulphur. But the iodine titration in the gas analysis revealed 0.36 cubic centimeter (at  $0^\circ$  and 760 millimeters) of sulphur gas whose odor was that of hydrogen sulphide rather than sulphur dioxide. If this were  $\text{H}_2\text{S}$ , it would diminish the amount of hydrogen which could have come from the reaction by 0.36 cubic centimeter; if, however, it were sulphur dioxide the volume of possible hydrogen would be swelled by 0.72 cubic centimeter in accordance with the reaction



But as there was certainly much more hydrogen sulphide than sulphur dioxide absorbed by the potassium hydroxide solution, it will be safe to balance the possible  $\text{SO}_2$  formed, by the  $\text{H}_2\text{S}$  undissociated, and ignore these corrections, which would probably reduce, rather than increase, the quantity of hydrogen which might result from pyrite.

If the iron had all been locked up in the mineral chalcopyrite ( $\text{CuFeS}_2$ ) the hydrogen might be accounted for, but chemical tests failed to detect the copper which this supposition would require. Just how much hydrogen might be expected from iron nitride ( $\text{Fe}_2\text{N}$ ) is not certain, since, in the presence of superheated steam, the nitrogen is more likely to unite with hydrogen and come off as ammonia rather than as free nitrogen, and ammonia is not dissociated short of the electric spark. That most of the iron in the quartz is in the form of a nitride is highly improbable. Iron carbide also would not yield sufficient hydrogen.

Another mineral apparently containing very little iron, but which yielded considerable hydrogen, was the beryl of analyses 101 and 101a.

Though as transparent as window-glass, one volume of this beryl contributed 0.31 volume of hydrogen. A determination of its accessible iron was made by pursuing the same method as was used for the quartz. The results were:

35.00 gms. beryl contained.....	0.0003 gm. $\text{Fe}_2\text{O}_3$
127.52 gms. beryl would contain.....	.00109 gm. $\text{Fe}_2\text{O}_3$
127.52 gms. beryl would contain.....	.00076 gm. Fe
Fe (as $\text{FeO}$ ) required to give 1 c.c. hydrogen.....	.00748 gm.
Maximum amount hydrogen from reaction.....	0.10 c.c.
Hydrogen actually obtained ( $0^\circ$ and 760 mm.).....	14.89 c.c.
Hydrogen not from this reaction.....	14.79 c.c.

This beryl expelled nearly 150 times as much hydrogen as can be assigned to the interaction of steam and ferrous oxide under the most generous assumptions. The actual hydrogen is 37 times the maximum quantity possible from this weight of iron, either as pyrite or in the metallic state. Here is a very declared case demonstrating the inadequacy of chemical reactions involving iron to generate the hydrogen obtained.

Heated in a closed tube with a limited amount of air, beryl is known to give up a small quantity of water which, in some varieties of the mineral, may reach 2 per cent. The question whether the excess of hydrogen over that possible from reactions between water and iron could have arisen from the dissociation of this water is easily answered. The recent researches of Nernst upon the dissociation of steam indicate that, at temperatures below  $2000^\circ\text{C}$ ., the process takes place only to a very limited extent. At  $1124^\circ\text{C}$ ., which is somewhat above the point to which the beryl was heated, only 0.0078 per cent of the total steam can be dissociated.<sup>1</sup> At this temperature, 127 grams of beryl containing 2 per cent of water should, on the basis of Nernst's figures, yield 0.24 cubic centimeter of hydrogen, provided the gas was quickly cooled. Hence only a small portion of the hydrogen can be attributed to the dissociation of water present in the mineral.

To the question of the importance of ferrous salts in the production of hydrogen, it is possible that meteorites, which have usually been regarded as free from water, can add testimony of some value. Though it is true that in freshly fallen specimens hydrous minerals have not yet been recognized,<sup>2</sup> nevertheless, the researches of Graham, Mallet, Wright, and Dewar, besides my analyses of the Allegan, Estacado, and Toluca meteorites, have shown that these bodies, when heated, give off much gas, rich in hydrogen. If these meteorites really contained no water, either original or by absorption from the earth's atmosphere, the hydrogen obtained from them can not be attributed to the decomposition of water; it must have been held within the mass of each meteorite, either entrapped or occluded.<sup>3</sup> But in several instances, at least, the investigators have stated that a certain quantity of water was driven off, though perhaps this came from weathered aerolites. The chemical analysis of the Allegan meteorite,

<sup>1</sup> Nernst, Chem. Central-Blatt, 1905, 2, p. 290.

<sup>2</sup> Farrington, Jour. of Geol., vol. 9 (1901), p. 532.

<sup>3</sup> It is to be remembered that a few meteorites have been found to contain hydrocarbons, from which hydrogen might arise, but the presence of these hydrocarbons from inorganic sources is more remarkable than that of hydrogen itself.

which was dug up while still hot, gave Stokes 0.25 per cent of water.<sup>1</sup> Perhaps this was moisture absorbed from the air by deliquescent compounds, such as lawrencite; still, on the other hand, there appears no reason, at the present time, why a part of this water should not be a primary constituent of the meteorite. This uncertainty points out the desirability of further, and more critical, studies upon the composition and properties of meteorites, before attempting to base an argument upon the absence of water in these bodies.

Other possible sources of hydrogen are hydrogen sulphide, hydrocarbons, and the products of radioactivity. As the decomposition of sulphureted hydrogen has already been mentioned, and is also treated under the head of that gas, it need not be discussed here. Hydrocarbons can only be represented in small quantities in igneous rocks, and should produce more methane than free hydrogen. Unless the analysis shows much marsh-gas, hydrogen from this source must be unimportant.

#### CARBON DIOXIDE.

The carbonates of most metals are decomposed by heat with the liberation of carbon dioxide. On this account the determination of the carbon dioxide yielded by rocks which have undergone much carbonation is of little value. Many rocks which appear to be perfectly fresh have nevertheless suffered slight carbonation while in the zone of weathering, and thus possess carbon dioxide in a combined state ready to be evolved when sufficiently heated. This carbon dioxide from the non-gaseous constituents of the rock embarrasses the determination of the free gas, since there is no way of separating the carbonic acid from these different sources.

The degree of heat necessary to decompose carbonates throws some light on the question. Erdmann and Marchand state that already at 400° traces of carbon dioxide are given off from calcium carbonate.<sup>2</sup> The studies of Debray show that at the boiling-points of mercury and sulphur, 350° and 448° respectively, the development of CO<sub>2</sub> from calcite in vacuo is inappreciable.<sup>3</sup> The same investigator found that at 860° calcite gives up carbonic anhydride until a pressure of 85 millimeters is reached, when the action ceases. At 1040° the pressure may rise to 520 millimeters before the evolution of gas is stopped. In the presence of carbon dioxide at the ordinary atmospheric pressure, calcite retains all of its optical and other properties unaltered, even at 1040°. Carbon dioxide from calcium carbonate is thus not of any quantitative importance below 450°. In general, most of the carbonic acid from the rocks is expelled at temperatures above 450°. But considerable CO<sub>2</sub> often appears before the heat reaches 400°, as is shown by the Baltimore gneiss. Perhaps this gas may be assigned to ferrous carbonate. Iron carbonate would be expected to decompose more readily than calcium carbonate, though I have been unable to discover at what temperature the process commences.

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<sup>1</sup> Ante, p. 21.

<sup>2</sup> Erdmann and Marchand, cited by Gmelin-Kraut, *Anorg. Chem.*, 2, p. 354.

<sup>3</sup> Debray, *Comptes Rendus*, vol. 64, p. 603.

When a finely powdered igneous rock is treated with hydrochloric acid and gently warmed, a few small bubbles of carbon dioxide usually are seen to rise to the surface of the acid. This gas comes from the action of the acid upon small quantities of carbonate present in the rock. To test the quantitative importance of this action and to discover whether other gases are freed by acid, 25.13 grams of diabase from Nahant, Massachusetts,<sup>1</sup> were placed in a flask connected with the mercury-pump, and the air removed. Dilute sulphuric acid was introduced into the flask through a dropping funnel. The gas developed in the cold during the first 2½ hours was found to have the following composition:

TABLE 35.

	Per cent.	Volumes.
Hydrogen sulphide .....	0.00	....
Carbon dioxide .....	98.10	6.44
Methane .....	.03	.00
Hydrogen .....	.25	.02
Nitrogen .....	1.62	.10
Total .....	100.00	6.56

Practically all of the carbon dioxide thus set free is to be assigned to a carbonate.

The apparatus was allowed to stand for three days, during which time more gas came off. At the end of this period, the powder was washed, dried, and then submitted to the ordinary process of heating in the tube. Of the gas received, 38.19 per cent, or 0.62 volume per volume of rock, was carbon dioxide. Powder from the same specimen of diabase, not treated with acid, yielded 8.51 volumes of carbonic anhydride in the combustion-tube. This amounted to 61.25 per cent of the total gas.<sup>2</sup>

While carbon dioxide, both gaseous and liquid, occurs in minute cavities in certain minerals and rocks, and while rocks also, doubtless, contain some of this gas in a state of occlusion, it seems probable, on account of the wide dissemination of carbonates in small quantities through the accessible rocks near the earth's surface, that the greater part of the carbon dioxide obtained by the method of heating rock material in vacuo is derived from the decomposition of carbonates in the combustion-tube. It may be assumed that more of the carbonates in igneous rocks are secondary than primary. But though a knowledge of this immediate source of much of the carbon dioxide in the rocks does not lead far toward the elucidation of the problem of the ultimate source of this gas, it imposes no restrictions upon the more comprehensive view that the carbonic acid which is now locked up in the rocks chemically, as a result of weathering and carbonation, was given to the atmosphere and hydrosphere originally from the magmas themselves.

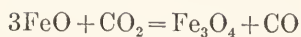
#### CARBON MONOXIDE.

Metallic iron and ferrous salts reduce carbon dioxide to monoxide under practically the same conditions that they liberate hydrogen from water-vapor.

<sup>1</sup> Analysis No. 88.

<sup>2</sup> Analysis No. 86.





While this action commences below  $400^\circ$ , it takes place slowly, and it is chiefly at higher temperatures that it becomes of quantitative importance. As in the case of hydrogen and water-vapor, this reaction is reversible, the direction in which it will proceed depending upon the proportions of the substances present. Either metallic iron or ferric oxide, heated in a mixture of equal parts of carbon monoxide and carbon dioxide, produces ferrous oxide.<sup>1</sup> Siderite at red heat passes into a magnetic oxide with the formation of both carbonic acid and carbonic oxide. According to Döbereiner this reaction takes place as follows:<sup>2</sup>



Glasson,<sup>2</sup> however, says that  $4\text{FeO} \cdot \text{Fe}_2\text{O}_3$  results, at first giving two parts of  $\text{CO}_2$  and one of CO, but that later the proportion changes to five parts of  $\text{CO}_2$  and one of CO.

It is, therefore, the normal thing for a rock containing carbon dioxide (whether occluded, or in cavities, or a carbonate) and iron in the ferrous condition to generate carbon monoxide on the application of heat. In this connection it may be noted that carbon monoxide rises very conspicuously in relative importance whenever there is metallic iron present in the material tested. The iron-bearing basalt of Ovikak, Greenland, gave 21.63 per cent of this gas compared with 46.50 per cent of the dioxide;<sup>3</sup> the Allegan meteorite, 38.61 per cent of CO and 41.74 per cent of  $\text{CO}_2$ ;<sup>4</sup> while the Estacado meteorite developed 29.31 per cent monoxide and only 28.47 per cent dioxide.<sup>5</sup> These were specimens of stony material containing grains of metallic iron. Quite different is the Toluca iron meteorite, whose nearly pure metal evolved 71.05 per cent carbonic oxide with but 6.40 per cent carbonic anhydride.<sup>6</sup> Wright's figures for iron meteorites are equally noted for high percentages of carbon monoxide.<sup>7</sup>

However, there are two other chemical sources for carbon monoxide, one of which is, perhaps, especially applicable to iron meteorites. It is known that the carbides of chromium and iron, when heated with the oxides of these metals, produce carbonic oxide.<sup>8</sup> As these meteorites often contain considerable carbon, some of it perhaps as a carbide, scrupulous care is always necessary in preparing the metal for the analysis, to avoid introducing any rust from the oxidized exterior of the mass.

The other principle must always be operative in the combustion-tube. Boudouard has shown that at the temperatures of the combustion-furnace hydrogen reduces carbon dioxide, forming carbon monoxide at the expense of both hydrogen and the dioxide.<sup>9</sup>

<sup>1</sup> Wright and Luff, Jour. Chem. Soc., vol. 33 (1878), p. 504.

<sup>2</sup> Cited by Gmelin-Kraut, Anorg. Chem., vol. 3, p. 319.

<sup>3</sup> Analysis No. 45.

<sup>4</sup> Analysis No. 106.

<sup>5</sup> Analysis No. 107.

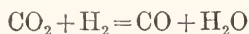
<sup>6</sup> Analysis No. 108.

<sup>7</sup> See p. 6.

<sup>8</sup> Borchers and McMillan, Electric Smelting and Refining, p. 545.

<sup>9</sup> O. Boudouard, Chem. Central-Blatt (1901), 1, p. 1350.



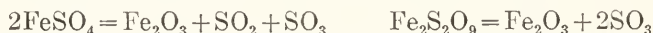


Equal volumes of hydrogen and carbon dioxide heated at  $850^\circ$  for one hour gave  $\text{CO}_2$  44.3 per cent,  $\text{CO}$  8.3,  $\text{H}_2$  42.0, and  $\text{H}_2\text{O}$  5.4 per cent. Heated for three hours under the same conditions, the proportion of carbon monoxide rose to 18 per cent. When rocks are heated for analysis, the gas is usually pumped off at short intervals, and this reaction, because of its slowness, becomes less important. Hüttner has appealed to this reaction to explain the presence of carbon monoxide in minerals.

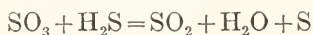
But metallic iron also has a penchant for absorbing carbon monoxide at the proper temperature. This process is usually called occlusion, and may perhaps partake of the nature of a combination in which the gas temporarily unites with the iron as iron carbonyl,  $\text{Fe}(\text{CO})_4$ ,<sup>1</sup> an unstable compound readily giving up carbonic oxide. It seems likely that a portion of the carbon monoxide developed from these irons, particularly those of meteoritic origin, actually exists in the iron as monoxide, and that not all of it has been formed by reduction of the dioxide.

#### SULPHUR DIOXIDE.

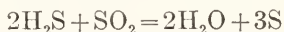
Certain rocks, when heated, disengaged sulphur dioxide in considerable quantities.<sup>2</sup> These were ferruginous rocks of rusty appearance, generally metamorphosed pyritiferous shales which had undergone much weathering. By oxidation, the original pyrite had been partially converted into ferrous sulphate ( $\text{FeSO}_4$ ) and basic ferric sulphate ( $\text{Fe}_2\text{S}_2\text{O}_9$ ), both of which were decomposed by the heat of the combustion-furnace.



The sulphur trioxide was reduced to the dioxide either by hydrogen sulphide, hydrogen, ferrous oxide, or sulphur.



It has been my observation that whenever sulphur dioxide was evolved a slight sublimate of sulphur collected toward the cool end of the tube. This may have been derived from the reaction above, or from hydrogen sulphide and sulphur dioxide, coming from ferrous disulphide and sulphate, respectively, and which can not exist together.



The sulphur dioxide obtained in the study of rocks is all assigned to these reactions, though it is not impossible that this compound may occur in small quantities, as a gas or a liquid, imprisoned in minute cavities.

#### HYDROGEN SULPHIDE.

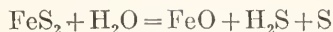
When iron pyrites ( $\text{FeS}_2$ ) is heated in a stream of hydrogen, ferrous sulphide ( $\text{FeS}$ ) and free sulphur result.<sup>3</sup> Though no hydrogen sulphide

<sup>1</sup> Fe and CO also exist feebly united in other proportions, as iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , and heptacarbonyl,  $\text{Fe}(\text{CO})_7$ .

<sup>2</sup> Analyses Nos. 43, 65, 93, and 109.

<sup>3</sup> Rose, Pogg. Ann., vol. 5, p. 533.

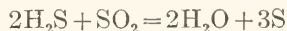
is formed in this manner, that gas is produced when pyrite is decomposed by steam at high temperatures.<sup>1</sup>



As pyrite is frequently present in igneous rocks which generally evolve water-vapor upon the application of heat, the limited quantities of hydrogen sulphide obtained may be explained in this way. But unless the hydrogen sulphide be removed, this process can proceed only to a certain point, for, according to Berzelius, iron disulphide is formed when  $\text{FeCO}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ , or  $\text{Fe}(\text{OH})_3$  is heated with hydrogen sulphide to temperatures between  $100^\circ$  and red heat.<sup>2</sup> At red heat, a current of dry hydrogen sulphide completely converts  $\text{Fe}_3\text{O}_4$  into  $\text{Fe}_3\text{S}_4$  in two hours, while a still further increase of temperature results in the formation of  $\text{FeS}$  and a deposit of sulphur.<sup>3</sup>

An inspection of the analyses shows that sulphureted hydrogen is rarely obtained in large amounts from igneous rocks. An average of 75 analyses from a wide range of rocks (but omitting bituminous shales) gave 0.59 per cent of this gas. But this figure is not a good working average, since it has been much influenced by the high sulphide percentage of a few individuals. Deducting the five highest of these, the remaining 70 analyses give an average of 0.27 per cent of hydrogen sulphide. In 19 cases out of the 75, this gas was entirely lacking.

While it is probable that not much of this gas was given off from the rock material in the first place, a portion of it doubtless disappeared before passing through the pump into the gas-receiver. At the temperature of the combustion-furnace, hydrogen sulphide is apt to be partially dissociated into its elements, thus swelling the already large volume of hydrogen present.<sup>4</sup> Gautier states that sulphur heated in a tube filled with hydrogen sulphide causes the decomposition of the gas with the result that its sulphur is added to the free sulphur, while hydrogen, nearly pure, remains.<sup>5</sup> When the rock has been considerably weathered, and some of the pyrite oxidized into iron sulphate, so that, in addition to hydrogen sulphide, sulphur dioxide is disengaged, the former gas will be partially or completely decomposed, depending upon the relative proportions of the two gases.



The bituminous shale from Newsom's Station, near Nashville, Tennessee,<sup>6</sup> yielded sulphureted hydrogen to the extent of 30.94 per cent of the total gas, which is equivalent to the unusual amount of 29.38 volumes of hydrogen sulphide from one volume of shale. A specimen of the well-

<sup>1</sup> With an excess of steam the reaction goes further:  $3\text{FeS}_2 + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 3\text{H}_2\text{S} + 3\text{S} + \text{H}_2$ .

<sup>2</sup> Berzelius, cited by Graham-Otto, *Anorg. Chem.*, 4, p. 718.

<sup>3</sup> Sidot, *Chem. Central-Blatt*, vol. 40 (1869), p. 1038.

<sup>4</sup> See p. 47.

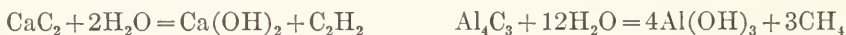
<sup>5</sup> Gautier, *Comptes Rendus*, vol. 132 (1901), p. 189. When pyrite is heated either in a vacuum, or in a stream of dry carbon dioxide,  $\text{Fe}_7\text{S}_8$  and free sulphur result (Berzelius, Rammelsberg, cited in Gmelin-Kraut, *Anorg. Chem.*, 3, p. 335).

<sup>6</sup> Analysis No. 41.

known "oil rock" from a lead and zinc mine near Platteville, Wisconsin, produced 6.79 per cent hydrogen sulphide, corresponding to 3.90 volumes per volume of rock.<sup>1</sup> How prolific a source of hydrogen sulphide the organic matter in certain shales may be, is indicated by these two experiments. If a shale of this sort, undergoing extensive metamorphism, did not lose all of its sulphur compounds during the transforming process, the metamorphic product might still be distinguished by a high content of hydrogen sulphide. Perhaps the specimen of Baltimore gneiss obtained from Spring Mill, on the Schuylkill River,<sup>2</sup> from which 4.91 per cent, or 0.30 volume, of sulphureted hydrogen was extracted, may have been derived from such a shale. Other sulphur compounds in small amounts have been noted in the gases from rocks. The potassium hydroxide solution in the Lunge nitrometer, after having absorbed whatever hydrogen sulphide and carbon dioxide there may have been in the gas under analysis, frequently emits an odor suggesting a mercaptan. When air is let into the pump and tubes, after the removal of the gas for analysis, and then pumped out, it usually is charged with odors of more or less offensive nature. These suggest that other complex reactions prevail at the high temperatures employed in extracting the gas. Gautier detected a trace of ammonium sulphocyanide in the gas from a granitoid porphyry from Esterel.<sup>3</sup>

#### METHANE.

Moissan believed that the hydrocarbons of the petroleum type which occur in the earth's crust were, in many cases, derived from the action of water upon metallic carbides in the deep interior.<sup>4</sup> His important researches upon carbides form the experimental basis for the hypothesis that the methane obtained by heating igneous rocks has resulted from these compounds. Even with cold water, the carbides of barium, strontium, calcium, and lithium give pure acetylene, while under the same conditions aluminum and beryllium carbides generate pure methane.



The carbides of the rarer metals, cerium, lanthanum, yttrium, and thorium, yield various mixtures of acetylene and marsh-gas; from manganese carbide, marsh-gas and hydrogen result. But the most remarkable of the carbides is that of uranium, which with water at ordinary temperatures produces (in addition to a gaseous mixture of methane, hydrogen, and ethylene) both liquid and solid hydrocarbons. Under ordinary conditions water does not decompose the carbides of molybdenum, tungsten, chromium, or iron.

These reactions suggest two alternative hypotheses to explain the occurrence of methane in the gas obtained from igneous rocks. The most limited of these supposes the marsh-gas to be produced from a carbide

<sup>1</sup> Analysis No. 42.

<sup>2</sup> Analysis No. 28.

<sup>3</sup> Gautier, *Comptes Rendus*, vol. 132, pp. 61-62.

<sup>4</sup> Moissan, *Proc. Roy. Soc.*, vol. 60 (1897), pp. 156-160.

in the combustion-tube. Such a carbide must have withstood the action of water, both magmatic and meteoric, ever since the solidification of the rock. The other hypothesis seeks to avoid this difficulty by postulating carbides in the very hot rocks where the hydrogen and oxygen may not be combined as water; then, at a later stage, it allows water to decompose the carbides with the evolution of marsh-gas, which is retained within the rock. In this case the gas itself would exist in the rock specimen tested.

It is to be noted that several of these carbides, including that of the widespread element calcium and the less stable sodium and potassium compounds,<sup>1</sup> give acetylene when decomposed by water. In none of the rocks examined, with one exception, has acetylene been detected. This may possibly eliminate calcium carbide from the gas-contributing compounds in the rocks. The absence of acetylene also carries with it some slight evidence against carbides in general, since calcium plays a very important rôle in rock evolution, and it is not likely that acetylene, if formed, would pass into methane. However, it is not impossible that aluminum carbide, which yields methane with water, may exist in the earth's crust while calcium carbide is lacking. According to F. W. Clarke,<sup>2</sup> aluminum constitutes 8.16 per cent of the solid crust of the earth, while iron and calcium comprise 4.64 and 3.50 per cent, respectively. Aluminum also forms very stable compounds in nature. Moreover, aluminum oxide fused in the electric furnace with calcium carbide gives yellow crystals of aluminum carbide.<sup>3</sup> Perhaps at high temperatures iron carbide might be decomposed by steam with the formation of marsh-gas.

Besides carbides, organic matter suggests itself as a possible source of the methane. This organic matter may have been either (1) accidentally introduced into the combustion-tube, or (2) have been incorporated in the rocks from life which inhabited the earth during the later stages of growth, as outlined by the planetesimal hypothesis. The first possibility may be practically dismissed, since great care was exercised to avoid the introduction of any foreign matter with the rock powder. If dependent upon such accidental conditions, this gas would only occasionally be present. Under the planetesimal hypothesis, life may have existed long before the growth of the planet was completed and its present size attained. Organic deposits buried in sedimentary beds which have since undergone extensive metamorphism should furnish marsh-gas. These rocks, worked over and reworked by the volcanic activity in Archean times, might perhaps account for the widespread occurrence of this gas. Formed in this way, it may be retained in the rocks as a free or occluded gas, since it is very stable at high temperatures.

Other theoretical sources of methane are high-temperature reactions within the combustion-tube, in which hydrogen and the oxides of carbon participate. Brodie produced 6 per cent of marsh-gas by submitting

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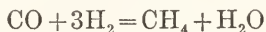
<sup>1</sup> Moissan, *Jour. Chem. Soc.*, vol. 64, 2, p. 332.

<sup>2</sup> F. W. Clarke, *Bull.* 168 U. S. G. S. (1900), p. 15.

<sup>3</sup> Moissan, *Comptes Rendus*, 125 (1897), pp. 839-844; *Jour. Chem. Soc.*, vol. 64 (1898), 2, p. 161.



approximately equal volumes of hydrogen and carbon monoxide to the action of electricity for five hours in an induction-tube.<sup>1</sup> From his results he expressed this reaction by the equation,



Though it is not safe to assume that this reaction will take place at the temperatures of the combustion-furnace, the observation that marsh-gas is obtained when a rock powder, exhausted of its gases, is exposed to the air for a few months, and reheated, possibly points toward some reaction of this nature.

#### NITROGEN.

If the nitrogen which is obtained from heating igneous rock powders in vacuo is derived from some chemical compounds decomposable at red heat, a metallic nitride at once suggests itself as the most probable form in which the nitrogen would occur. Iron nitride may be taken as the type for discussion. While different nitrides of iron, having the compositions of  $\text{Fe}_2\text{N}_2$ ,  $\text{Fe}_2\text{N}$ , and  $\text{Fe}_5\text{N}_2$ , have been described by some authors, a comprehensive study, by Fowler, of this formerly little-known compound, forces the conclusion that there exists<sup>2</sup> only one iron nitride,  $\text{Fe}_2\text{N}$ . This compound may be prepared by the action of ammonia either upon ferrous chloride, or finely divided iron. While the action between ferrous chloride and ammonia commences near the melting-point of lead ( $327^\circ$ ), a temperature of  $600^\circ$  appears to be necessary for the production of iron nitride in quantity.<sup>3</sup> The nitride can also be produced at  $850^\circ$  to  $900^\circ$ , but this is probably the highest limit of the reaction.<sup>4</sup>

This nitride is very soluble in dilute acids, giving ammonia. When heated to redness in hydrogen, ammonia results. At  $200^\circ$  it is oxidized in the air to ferric oxide, abandoning nitrogen, which does not appear to be oxidized. At  $100^\circ$  steam causes a slight evolution of ammonia. According to Fowler the temperature of decomposition of iron nitride in an inert gas (nitrogen) must certainly be above  $600^\circ$ .

Silvestri has found iron nitride coating some of the fumarole deposits of Etna,<sup>5</sup> and Boussingault<sup>6</sup> recognized nitrogen in the Lenarto meteorite by certain tests which led him to believe that it existed there as a metallic nitride. Silvestri discovered that at red heat the nitride from Etna was decomposed, delivering up its nitrogen. His experiments showing that iron nitride may be prepared artificially, by igniting the ordinary lava in a current of ammonium chloride vapor, probably illustrate what takes place in the fumaroles. But this nitride, which derives its nitrogen from ammonia or ammonium salts, in no way requires the existence of nitrides within the magma itself, except as a possible source for the nitrogen which unites with hydrogen to form the ammonia. There is danger in transferring the characteristics of fumarole deposits, which are formed

<sup>1</sup> Sir B. C. Brodie, *Proc. Roy. Soc.*, vol. 21 (1873), p. 245.

<sup>2</sup> Fowler, *Jour. Chem. Soc.*, vol. 79 (1901), pp. 285-299.

<sup>3</sup> Fowler, *Chem. News*, vol. 82 (1900), p. 245.

<sup>4</sup> Beilby and Henderson, *Jour. Chem. Soc.*, vol. 79, p. 1245.

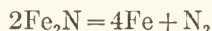
<sup>5</sup> Silvestri, *Pogg. Ann.*, vol. 157 (1876), pp. 165-172.

<sup>6</sup> Boussingault, *Comptes Rendus*, vol. 53 (1861), pp. 78-79.

in limited quantities under the quite exceptional conditions of abundant currents of free gases and very active hot vapors, to the main magmas.

If the nitrogen obtained from rock powders be derived from a nitride, it should be accompanied by ammonia, since, in the presence of hydrogen or water-vapor, it is this gas, rather than free nitrogen, which is given off. Tests made with Nessler's solution show that ammonia is one of the gases extracted from rocks, though always appearing in limited amounts. In the process ordinarily employed for extracting the gas, it is absorbed by the calcium chloride drying-tube. Ammonia is scarcely to be considered as a source of free nitrogen, since this compound is only dissociated at the temperature of the electric spark.

Whether all of the free nitrogen can be assigned to the decomposition of iron nitride may be tested with the quartz from New South Wales.<sup>1</sup> Supposing all of the iron in this quartz to have existed as iron nitride, and to have been completely decomposed without the production of any ammonia, the analysis still shows an excess of nitrogen over what could have been produced in this way. The reaction may be taken as



102.72 gms. quartz contained.....	0.0058 gm. Fe
Fe (as $\text{Fe}_2\text{N}$ ) required to give 1 c.c. nitrogen.....	.0100 gm.
Nitrogen possible from reaction.....	.58 c.c.
Nitrogen actually obtained ( $0^\circ$ and 760 mm.).....	.86 c.c.
Excess of nitrogen.....	.28 c.c.

A duplicate determination of the iron in this weight of quartz gave only 0.0048 gram; on this basis, the excess of nitrogen would be still greater. It is highly improbable that all of the iron in this quartz was combined as a nitride. Some of it was unquestionably pyrite. To ascertain how much of this nitrogen can be ascribed to atmospheric air adhering to the tubes, as well as to leakage during the process of extraction, a blank combustion was resorted to. The empty combustion-tube was kept at bright-yellow heat for the length of time which was required to expel the gas from the quartz. 0.15 cubic centimeter of gas was collected in the receiver when the tube was exhausted by the pump. Adhesion of air to the quartz itself might be supposed to increase this figure, though the material used for this analysis was not the usual fine powder, but small fragments which would be less liable to entrap air. In general, while iron nitride is to be accepted as a possible source of this nitrogen, it is inadequate to produce the quantities of this gas determined by analysis. The presence of other metallic nitrides in this comparatively pure quartz does not seem likely. Silicon nitride, however, may be present and might possibly contribute a portion of the nitrogen.

#### OCCLUDED GASES.

Though occlusion is a phenomenon but imperfectly understood, there appear to be three different ways in which it is manifested. In the first of these the absorption seems to be dependent upon porosity. An example of this is charcoal, one variety of which absorbs 172 volumes of ammonia,

<sup>1</sup> Analysis No. 100.

165 volumes of hydrogen chloride, 97 volumes of carbon dioxide, and 2 volumes of hydrogen.<sup>1</sup> The affinity of molten silver for oxygen illustrates another phase of absorption often classed as occlusion. It has long been known that silver absorbs 22 times its own volume of oxygen when melted, but gives up most of this gas, often with violence, as it solidifies.<sup>2</sup> This is properly a solution of a gas in a liquid, and not in a solid, as in the case of true occlusion. The third type is the absorption of gases by compact metals, either on their surface or within their mass, such as the occlusion of hydrogen by palladium, platinum, and iron. This is, in the main, independent of porosity.

Hydrogen is absorbed by these metals at ordinary temperatures, but is only given off at higher temperatures. This principle was demonstrated by Graham, who placed a thin plate of palladium, charged with hydrogen, in a vacuum and observed that at the end of two months the vacuum was still perfect. No hydrogen had vaporized in the cold, but on the application of a heat of 100° and upwards, 333 volumes of gas were evolved from the metal.<sup>3</sup> The degree of heat required to expel hydrogen absorbed by platinum and iron was found to be little short of redness, although the gas had entered the metal at a low temperature. Another series of experiments by the same investigator showed that, to be occluded by palladium and even by iron, hydrogen does not need to be applied under sensible pressure, but on the contrary, when highly rarefied, it is still freely absorbed by these metals. These results have been confirmed by Mond, Ramsay, and Shields,<sup>4</sup> who found that platinum black at very low pressures absorbed a certain quantity of hydrogen. On increasing the pressure of the hydrogen up to about 200 to 300 millimeters, a further quantity was absorbed, but beyond this point an increase of pressure had comparatively little effect. These investigators regarded 110 volumes as the amount of hydrogen really occluded by platinum black, although 310 volumes were actually absorbed.

Experiments indicate that the quantity of hydrogen occluded depends greatly upon the condition of the metal. When chemically reduced, cobalt may occlude 59 to 153 volumes, nickel 17 to 18, and iron 9 to 19 volumes.<sup>5</sup> Though common iron wire occludes only 0.46 volume of hydrogen,<sup>6</sup> this same metal, when electrolytically deposited, may absorb nearly 250 volumes of this gas.<sup>7</sup> The maximum quantity of hydrogen occluded by any metal, so far as recorded, is 982 volumes absorbed by freshly precipitated palladium.<sup>8</sup> Dumas has shown that aluminum heated in vacuo to 1400° gives off more than its own volume of gas, consisting chiefly of hydrogen with a little carbon monoxide, but without traces of carbon dioxide, oxygen, or nitrogen.<sup>9</sup> Under the same conditions, magnesium rapidly expels 1.5

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<sup>1</sup> Barker, *Textbook of Physics*, p. 183.

<sup>2</sup> *Chimie Minérale*, Moissan, t. 1, p. 203.

<sup>3</sup> Graham, *Chemical and Physical Researches*, pp. 283-290.

<sup>4</sup> *Proc. Roy. Soc.*, vol. 58 (1895), pp. 242-243.

<sup>5</sup> *Chimie Minérale*, Moissan, t. 1, p. 51.

<sup>6</sup> Graham, *Chemical and Physical Researches*, p. 279.

<sup>7</sup> Caillietet, *L'Institut, Nouv. Sér.*, Ann. 3, p. 44.

<sup>8</sup> Graham, *Chemical and Physical Researches*, p. 287.

<sup>9</sup> Dumas, *Comptes Rendus*, 90 (1880), p. 1027.

volumes of nearly pure hydrogen. Many other metals behave similarly. Non-metallic substances appear to possess this property in a lesser degree. Porcelain occludes hydrogen, whether because of its porosity or solvent qualities is not certain. Quartz is said to be penetrable, at high temperatures, by the gases from the oxyhydrogen flame,<sup>1</sup> which points towards a form of occlusion.

In addition to hydrogen, other gases are occluded. Litharge, when in the molten condition, dissolves hydrogen, carbon monoxide, and nitrogen, of which it retains a portion on solidifying.<sup>2</sup> Cast iron, on cooling, retains 4.15 volumes of carbon monoxide,<sup>3</sup> which perhaps may be due to the formation of iron carbonyl,  $\text{Fe}(\text{CO})_4$ , or similar unstable compounds.

Analyses show that whenever metallic iron is present in notable quantities carbonic oxide becomes an important constituent of the gas evolved. The following analyses of the gases from various types of iron indicate the proportions of hydrogen, carbon monoxide, carbon dioxide, and nitrogen which this metal may absorb, given in percentages of the total gas content:

TABLE 36.

Iron.	Analyst.	H <sub>2</sub> .	CO.	CO <sub>2</sub> .	N <sub>2</sub> .
White, carbonaceous, cast iron.....	Troost & Hautefeuille <sup>1</sup>	74.07	16.76	3.59	5.58
Mild steel .....	Parry	52.6	24.3	16.55	6.5
Ordinary gray charcoal iron .....	Cailletet	38.60	49.20	....	12.20
Gray coke iron .....	Do	32.70	57.90	....	8.40
Steel .....	Troost & Hautefeuille	22.27	63.65	2.27	11.36
Bessemer steel before adding spiegel....	Müller <sup>2</sup>	88.8	0.7	....	10.5
Bessemer steel after adding spiegel .....	Do	77.0	....	....	22.9
Open-hearth steel .....	Do	67.8	2.2	....	30.8
Cupola pig iron .....	Do	83.3	2.5	....	14.2
Horseshoe nail, heated 2 hours .....	Graham <sup>2</sup>	35.0	50.3	7.7	7.0
Same, heated 2 hours more .....	Do	21.0	58.0	....	21.0

<sup>1</sup> Cited by Cohen, *Meteoritenkunde*, p. 181.

<sup>2</sup> Cited by Lane, *Bull. Geol. Soc.*, vol. 5 (1894), p. 264.

Whatever may prove to be the ultimate significance of occlusion, and in whatever condition these gases are stored in the iron, whether it be in the nature of a solution, as Mendeléef has suggested, or as definite compounds—hydrides, nitrides, and carbonyls—the fact remains that these gases exist within the metal and are in many respects similar to the gases locked up in iron meteorites. Fresh iron borings from the interior of a metallic meteorite have usually been assumed to be free from any hydration or carbonation from terrestrial agencies, and so have been held to contain true meteoritic gases. Some question respecting this belief has arisen from certain analyses which, as we have seen, indicate secondary action.<sup>4</sup> In addition to this the gases actually received in the laboratory may not represent the original

<sup>1</sup> Poynting and Thomson, *Properties of Matter*, p. 204.

<sup>2</sup> Le Blanc and Cailletet, cited by Violle, *Cours de Physique*, t. 1, p. 922.

<sup>3</sup> Daniell, *Principles of Physics*, p. 327.

<sup>4</sup> Experiments with the Toluca iron; Analysis No. 108.



proportions on account of the reducing action of iron on carbon dioxide and water-vapor. Meteorites of the stony type, unless absolutely fresh, are more open to the suspicion of terrestrial hydration and carbonation. But the Allegan meteorite gathered up, still hot, within five minutes of its fall, has not been subjected to outdoor exposure, though it may have absorbed a small amount of moisture and carbonic acid from the atmosphere since being placed in the National Museum. It yielded somewhat more than half of its own volume of gas.<sup>1</sup> Fresh material from the interior of the Estacado, Texas, meteorite, heated in a vacuum in the presence of phosphorus pentoxide for five hours at 150°, and then allowed to remain untouched for several days to enable the drying agent to take up the last traces of moisture in the tubes, still yielded at red heat 0.86 volume of gas, of which 36.25 per cent was hydrogen.<sup>2</sup>

These gases from stony meteorites resemble those from some igneous rocks. That this correspondence should exist, is entirely in accordance with the view that meteorites have been derived from the disruption of small planetary bodies of the nature of the asteroids. As in the meteorites, so in the rocks, that portion of the gases which can not have been produced by chemical reactions at elevated temperatures, nor from the bursting of rock-bound cavities, may fairly be assigned to occlusion. The computations indicating the excess of hydrogen obtained from quartz and beryl<sup>3</sup> over that which might have arisen from the interaction of iron and water under the most generous assumptions show that, in some cases, more gas may arise from a state of occlusion than from ordinary chemical action. The amount of occluded gases may be actually greater than that indicated by demonstrating the inadequacy of other modes of holding gas. But in basic rocks containing hydrated minerals and an abundance of ferrous salts, the resulting volumes of hydrogen must doubtless come largely from the decomposition of the water of constitution, and the amount of occluded gases, if any, is beyond determination by these methods.

The gases argon and helium, which, according to current chemical views, do not form compounds, must exist within rocks either mechanically entrapped or in a state of occlusion. There are those, notably Ramsay and Travers, who believe in the combining properties of argon and helium; but the balance of opinion seems to be on the other side, so far as ordinary terrestrial conditions are concerned. Lord Rayleigh concludes his paper on the inactivity of these two gases, with this sentence: "There is, therefore, every reason to believe that the elements, helium and argon, are non-valent, that is, are incapable of forming compounds."<sup>4</sup>

As the chemists' supply of helium comes from certain minerals, chiefly those containing compounds of uranium, its occurrence in rocks is a well-known fact. Recent studies have revealed the existence of helium in beryl.<sup>5</sup> Argon is perhaps more widely distributed than helium, Gautier having detected this element in ordinary granite. The waters of many springs

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<sup>1</sup> Analysis No. 106.

<sup>2</sup> Analysis No. 107.

<sup>3</sup> Ante, pp. 46-48.

<sup>4</sup> Lord Rayleigh, Proc. Roy. Soc., vol. 60, p. 56.

<sup>5</sup> R. J. Strutt, Nature, Feb. 21, 1907, p. 390.

bring up both helium and argon, proving the presence of considerable quantities of these elements within the earth. This rather wide distribution, when taken in connection with their supposed chemical inertness, strengthens the presumption that occlusion, or some form of gas diffusion, is prevalent in rocks. Though of much interest to chemists and physicists, these gases, on account of their comparative scarcity, do not play a very important rôle in general geological problems. Their presence in small quantities within the rocks of the earth's crust being established, quantitative determinations become of less value. In the analyses made for this paper, whose prime purpose was to determine the range and distribution of the common gases, the separation of helium and argon from nitrogen was not usually attempted. These gases when present are included in the figures given for nitrogen. In the case of pitchblende and carnotite, however, helium was so important a constituent of the gas that its proportions were determined. Carnotite produced 1.28 per cent of helium, amounting to 0.04 volume, while pitchblende gave 38.48 per cent, or 0.37 volume.<sup>1</sup> In both of these cases nitrogen also was abnormally high.

In general, therefore, helium and argon, together with at least as much of the other gases as can be shown not to have been produced by chemical reactions or the bursting of inclosing walls, are to be attributed to occlusion or some form of diffusion not distinguishable from occlusion. In many, and perhaps most, rocks this will not be the major part, for, of the three gas-liberating processes, that by chemical interaction under the influence of heat appears to be the dominating one.

## SIGNIFICANCE OF THE THREEFOLD STATE.

### GAS IN CAVITIES.

While chemical reactions and the phenomena of occlusion imply that gas exists in the interior of the earth, the presence of gas inclosed in cavities under great pressure adds the further implication that the gas often exceeded the point of saturation of the magma, at least at the stage of solidification. Cavity gases are most abundant in minerals of poorly developed cleavage, pointing perhaps towards a strong tendency to escape along cleavage planes during, or after, crystallization. The gas inclusions in quartz may, however, owe their abundance not so much to the absence of cleavage as to the fact that quartz is generally the last mineral to crystallize out of a magma, and hence such absorbed gases as did not enter into the other crystals would become concentrated in the siliceous residue and might supersaturate it.

It is possibly this freely-moving gas above the point of saturation which contributes most to the mobility of lavas. Dissolved gases and vapors, while favoring fluidity, would seem to be relatively less effective. But the foregoing investigations imply that gases mechanically entrapped in crystalline rocks are not very abundant, and suggest that perhaps the theory of liquidity due to gas is overworked. On the other hand, it is true that as the lava cooled down to the point where the last mineral crys-

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<sup>1</sup> Analyses 93 and 94.

tallized, its gas-solvent powers would be increasing, allowing some of the gas to pass into solution. At the same time free gas might be occluded by the growing crystals. The experiments upon the reabsorption of gas by exhausted rock powder indicate that a portion of the gas unites chemically as the heat diminishes. Because of these processes, liquid lavas may be supplied with free gas, even when the solidified rocks retain but little free gas.

As the imprisoned carbon dioxide frequently remains in the liquid form up to the critical point (30.9° C.), it must be subjected to a pressure of at least 73 atmospheres, which is the critical pressure of this gas. Since a pressure of 73 atmospheres corresponds to a column of water 2,470 feet in height, quartz crystals formed from aqueous solution, under hydrostatic pressure simply, can not contain liquid carbon dioxide up to 30.9° unless developed at depths exceeding 2,470 feet. It is to be recognized, however, that such crystals might be formed at lesser depths if mechanical pressure operated with hydrostatic pressure or replaced it.

If the quartz crystallized from a lava, say at 1100° C., the effect of cooling down to ordinary temperatures upon both the size of the cavity and the pressure of the inclosed carbon dioxide must be taken into account. If we take the case of a cavity found to be entirely filled with carbon dioxide at the critical point (30.9° C. and 73 atmospheres), it is possible, by the use of Van der Waal's equation, to calculate the pressure to which the gas would be subjected if the quartz were heated to 1100°. This pressure is found to be 756 atmospheres,<sup>1</sup> provided the size of the cavity remains constant. But as most minerals contract on cooling, the volume of the cavity diminishes at the same rate as though it were filled with the material of the inclosing walls.<sup>2</sup> The coefficient of expansion of quartz is given as 0.00003618. Assuming for the sake of simplicity that the rate of expansion does not vary greatly with changing temperatures,<sup>3</sup> quartz, cooling from 1100° to 31°, would contract to an extent of about 3.87 per cent of its original volume. Since the contraction of the quartz diminishes the size of the cavity and increases the pressure by 3.87 per cent, the original pressure need be only 727 atmospheres, which corresponds to the pressure beneath 9,100 feet of average rock. To fill cavities forming in crystals at 1100° with carbon dioxide which is so condensed that it will pass into the liquid state just at the critical temperature when the rock cools down, a pressure corresponding to a depth of at least 9,100 feet, or its mechanical equivalent, would seem to be required. If, when warmed under the microscope, the liquid carbon dioxide is found to pass into the gaseous state at temperatures below 30.9°, and the cavity contains only carbon dioxide, or carbon dioxide and water, these must have been entrapped under a pressure less than 727 atmospheres, or else the crystal was formed at a temperature above 1100°.

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<sup>1</sup> By starting with the equation  $p = \frac{RT}{v-b} - \frac{a}{v^2}$  at the critical point where the values of the constants are taken as  $R=0.003684$ ;  $a=0.00874$ ;  $b=0.0029$ ;  $v=3b=0.0087$ , and substituting for the critical temperature,  $T=1100^\circ+273^\circ$ , the theoretical value of 756 atmospheres for the pressure at 1100° is obtained.

<sup>2</sup> Daniell, Principles of Physics, p. 379.

<sup>3</sup> It would, however, slowly increase with the increase of temperature.



The estimate of 9,100 feet for the minimum depth (where weight alone acts) at which igneous quartz crystals now containing carbon dioxide, liquid up to  $30.9^\circ$ , could have been formed,<sup>1</sup> applies best to those cases in which only carbon dioxide exists in the crystal cavities. If there are other gases and liquids present in appreciable quantities, this figure becomes less applicable, since the constants  $a$  (denoting an internal force or attraction) and  $b$  (representing the sum of the spheres of influence of all the molecules in the space  $v$ ) used in Van der Waal's equation are not the same for all gases. At how much greater depths than this the crystallization of certain specimens of quartz actually did take place, if rock weight alone was involved, may, perhaps, be estimated by a painstaking determination of the pressure under which the imprisoned carbon dioxide exists in these minute cavities. This might be accomplished by piercing one of the larger cavities while submerged in mercury or other liquid, and noting the expansion of the freed bubble, as first suggested by Sir Humphry Davy.

Though naturally subject to limitations, it is nevertheless possible to throw considerable light upon the nature of cavity inclusions by the use of the microscope. Some of the conditions may be stated:

(1) If, at slightly under  $30.9^\circ$ , the cavity is entirely filled with a liquid which completely vaporizes at  $30.9^\circ$ , it contains only carbon dioxide.

(2) If, at slightly under  $30.9^\circ$ , the cavity is filled with two immiscible liquids, one of which passes into the gaseous state at  $30.9^\circ$ , the liquids are probably water and carbon dioxide.

(3) If the cavity, when just below  $30.9^\circ$ , contains a liquid and an appreciable gas-bubble, and the liquid does not disappear when the slide is warmed above  $30.9^\circ$ , the liquid is probably water, and the bubble water-vapor with perhaps some of the difficultly liquefiable gases, such as hydrogen, nitrogen, or methane.

(4) If, as is often the case, the temperature at which the liquid in a cavity disappears is found to be several degrees below the critical temperature of carbon dioxide, two interpretations are possible: either the carbon dioxide is subject to a pressure less than 73 atmospheres, or else there is a small proportion of another less liquefiable gas present. If the cavity be opened and only carbon dioxide be found, the pressure under which the gas existed, and from that something as to the conditions under which the crystal was formed, can be computed from the temperature at which the liquid disappeared. If another gas, such as hydrogen or nitrogen, be found and identified, it is possible, by using an equation,<sup>2</sup> to calculate the relative proportions of the two gases from the critical temperature of the mixture. Thus a cavity containing a mixture of carbon dioxide and nitrogen which had a critical temperature of  $29^\circ$  would hold 98.7 per cent

<sup>1</sup> This figure is based on the assumption that the quartz crystallized at  $1100^\circ$ ; if it is desired to use other temperatures, they can be substituted in Van der Waal's equation and the corresponding pressures computed.

<sup>2</sup>  $t = \frac{nt_1 + (100 - n)t_2}{100}$ , where  $t$  is the observed critical temperature of the mixture,  $t_1$  and  $t_2$  are the theoretical critical temperatures of the two liquefied gases. Then  $n$  equals the proportion by weight of the first liquid and  $100 - n$  equals the proportion by weight of the second liquid.



of the former and 1.3 per cent of the latter. A critical temperature of 28° would indicate 98.1 per cent of liquid carbon dioxide and 1.9 per cent of liquid nitrogen, while 27° would mean 97.5 per cent of the dioxide and 2.5 per cent nitrogen. The figures for carbon dioxide and hydrogen are of the same general order. In the estimates of the depths at which cavity-bearing crystals were formed, made by different methods,<sup>1</sup> it has been usual to assume that only the pressure arising from the weight of the overlying rock was involved.

Sorby examined those cavities which contained only water, or a saline solution, and a vacuole left by the contraction of the liquid, as a result of the lowering of the temperature. By noting the relative size of the bubble and the volume of the liquid, he estimated the temperature to which the mineral would have to be heated for the liquid to completely fill the cavity, and from this, together with the elastic force of the water-vapor, he computed the necessary existing pressure in feet of rock. The highest temperature found by this method was only 356° C., at which point Sorby believed that the trachyte of Ponza solidified, while the lowest temperature was 89° C., obtained from a study of the main mass of granite at Aberdeen. But Sorby considered it more probable that the granite crystallized at about the same temperature as the trachyte and, assuming that the solidification took place at 360°, he computed that the granite of Aberdeen was formed under a pressure of 78,000 feet of rock.<sup>2</sup> These estimates are based upon the unwarranted supposition that when the crystals were formed the volume of liquid water was such as to just fill the cavities, and that in each case a meniscus *at once* appeared with a loss of heat. He overlooked the fact that the meniscus could not appear until the water reached the liquid condition, no matter at what temperature the growing crystal surrounded the vesicle of highly compressed water-gas.

The highest temperature at which a vacuole of this sort can appear must, therefore, be the critical temperature for water, or 365° C. In order to study this problem, we may, perhaps, best take the special case in which the inclosed water passed through its critical state (at 365° and 200.5 atmospheres pressure) during the cooling of the crystal. The vesicle formed in this case may be termed the critical vacuole. It may be assumed that the growing crystal inclosed the water at some temperature in the neighborhood of 1100°, which is an average temperature for the solidification of lavas. Starting thus with a cavity formed at 1100°, in order to allow the water on cooling to pass through the critical state, an original pressure of 1,070 atmospheres is necessary according to Van der Waal's equation,<sup>3</sup> provided the size of the cavity remained constant. But if 2.66 per cent is allowed for the shrinkage of the cavity while cooling down<sup>4</sup> from 1100°

<sup>1</sup> See Geikie's Textbook of Geology, vol. 1, pp. 144-145.

<sup>2</sup> Sorby, Quart. Jour. Geol. Soc. London, vol. 14, p. 494.

<sup>3</sup>  $p = \frac{RT}{v-b} - \frac{a}{v^2}$ . In this case the values of the constants for the critical point were taken to be  $R=.003607$ ;  $a=.01173$ ;  $b=.00151$ ;  $v=3b=.00453$ . By substituting for the critical temperature,  $T=1100+273$ , the equation gives the theoretical value of 1,070 atmospheres.

<sup>4</sup> Ante, p. 62.

to 365°, the original pressure need be only approximately 1,040 atmospheres, a pressure which corresponds to 13,000 feet of rock approximately.

In this critical case the meniscus appears as soon as the temperature falls below 365°. Since pressure exerts but little influence on the volume of liquids, the shrinkage of the water in the cavity, and hence the growth of the gas-bubble, is largely a function of the fall in the temperature, and, with a knowledge of the varying coefficient of expansion, the relation between the size of the bubble and the volume of the liquid could be computed for any temperature. The correction for the constriction of the cavity between 365° and 20° amounts to a little more than one per cent, which is to be added to the size of both the cavity and the vacuole in computation.

If these principles be true, a vapor-bubble relatively smaller than the critical vacuole may be interpreted to mean that the meniscus did not appear in the cavity until the crystal had cooled below the critical temperature, *i. e.*, that at this temperature the water was more than normally condensed, owing to a pressure exceeding the critical pressure. On the other hand, a vapor-bubble relatively larger than the critical vacuole means that, although it did not appear until below 365°, it began as a sizable vesicle when it did start, owing to the lower pressure and more rarefied condition of the water-gas.

On the basis of his experiments, Sorby estimated that a vesicle amounting to 28 per cent of the volume of the liquid in the cavity would vanish when the water was heated to 340° C. According to this figure, a vacuole occupying in the neighborhood of 30 or 35 per cent of the volume of the liquid should correspond to a shrinkage of the water from the critical point to ordinary temperatures. But this figure has not been confirmed by other investigators. Unfortunately the figures obtainable for the expansion of water up to the critical point vary within such wide limits that it does not seem advisable at the present time to attempt to calculate the relative sizes of the critical vacuole and the inclosing liquid.

The difficulties involved in applying these principles are considerable. Zirkel has pointed out that, even in cavities within the same crystal, there is much variation in the relative volume of the vapor-bubble and the liquid, from which the inference is drawn that the vapor-bubbles are due to causes other than contraction on cooling.<sup>1</sup> Before this conclusion can be accepted with confidence, due consideration must be given to the location of the cavities within the crystal, and also to the evidence that they are all primary inclusions. In an ascending lava subject to a steadily diminishing pressure, those cavities formed during the early stages of crystallization may be developed under conditions quite different from the cavities later inclosed in the outer parts of the crystals. If systematic differences in the cavities can be found to correspond with variations in their location, something might be learned of the history of the lava during the period of crystallization. Secondary fluid inclusions, formed subsequent to the solidification of the magma, must obviously be recognized and avoided, whenever possible, in attempting to estimate the conditions under which crystallization took place.

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<sup>1</sup> Zirkel, cited by Geikie, *Textbook of Geology*, 1, p. 145.

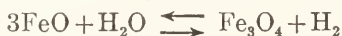
A difficulty of a more serious nature, apparently, suggested by Professor Iddings, lies in the change of volume of the magma in the passage from the liquid to the crystalline form. Some magmas, such as those of granitic rocks, contract so appreciably upon crystallization that it is conceivable that the last crystals to form, those of quartz (which also contain the most liquid and gas inclusions) might crystallize under reduced pressures in spaces inclosed by crystals of the minerals already formed. The relative size of the bubble of vapor in the cavity and the accompanying liquid would, in such cases, not correspond directly to the depth beneath the surface at which crystallization took place, even when nothing but hydrostatic pressure affected the lava column.

In the present defective state of knowledge as to the modes and conditions which obtain in lavas penetrating the shell of the earth, it is by no means safe to assume that the pressures to which an igneous intrusion is subject are merely those represented by the overlying rock or a lava column reaching to the surface. An ascending tongue of lava may extend to great depths and be affected by pressures brought to bear upon it in its lower part, which might be in excess of those represented by the depth of the head of the column, to an unknown degree. So also it is possible that lavas may become involved in mechanical deformations and thus be subject to special pressures in no close correspondence to their depth.

#### WATER AND HYDROGEN.

The reversible reactions involving hydrogen, water, and iron compounds, which cause uncertainties in the extraction of gases by heat, are also operative within the earth. In the laboratory, when either ferrous salts and water, or ferric compounds and hydrogen, are heated in tubes without the removal of the products, reversible reactions set in until a condition of equilibrium is established. Hydrogen and water, ferrous and ferric salts are all present in a state of balance. In the interior of the earth the heated, though solid, rocks should, it would seem, behave similarly, though hindered by the slowness of diffusion. Nor should liquid magmas constitute any exception to the law. Both hydrogen and water-gas, theoretically, should be present in liquid magmas and heated solid rocks. The chief uncertain factors are high temperatures, and pressures.

The effect of pressure on chemical equilibrium is to favor the formation of that system which occupies the smaller volume, but if there is no change in volume, in passing from one system to the other, the increase of pressure presumably has no influence on equilibrium.<sup>1</sup> In the reaction



considered as a thermochemical equation, the number of gaseous molecules, and hence the volume of gas, always remains the same, so that it is not likely that this action will be influenced by change of pressure. A rise of temperature favors the formation of that system which absorbs heat when it is formed.<sup>2</sup> A comparison of the amount of heat liberated by oxidizing three molecules of FeO to Fe<sub>3</sub>O<sub>4</sub> and one molecule of H<sub>2</sub> to H<sub>2</sub>O

<sup>1</sup> Jones, *Physical Chemistry*, p. 514.

<sup>2</sup> Van't Hoff, *Lectures on Theoretical and Phys. Chem.*, Pt. 1, pp. 161-164.



shows that, in the former case, 73,700 calories are evolved, and in the latter 58,300; that is,  $3\text{FeO} + \text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 + 15,400$  calories. As heat is evolved in this process, a rise of temperature would accelerate the reaction in this direction less than the reverse. In other words, the higher the temperature, the more would the formation of ferrous oxide and water be favored as compared with the conditions at lower temperatures.

Because of this, there is much reason to suppose that, at the depths where lavas originate, hydrogen and oxygen exist combined as water, since up to temperatures of  $2000^\circ\text{C}$ ., the dissociation of water takes place only to a limited extent. If a state of equilibrium between hydrogen, water, and the iron compounds were established in the heated interior where a magma originated, as soon as it commenced its way upward and began to lose heat the condition of equilibrium would be destroyed. With the falling temperature, the tendency to reestablish equilibrium would favor the formation of that system which was produced with the liberation of heat, *i. e.*, magnetic oxide and free hydrogen. In ascending lavas which are losing heat, the tendency, therefore, is to produce hydrogen and magnetite, or ferroso-ferric compounds. This is doubtless an important source for the hydrogen which is so copiously exhaled during a volcanic eruption. At the same time, this process accounts for the widespread occurrence of magnetite in igneous rocks. The considerable deposits of magnetite, formed apparently from magmatic segregation, which are common in various regions, may, perhaps, owe their origin to a combination of causes, in which this equilibrium reaction is an important factor.

In general, these reversible reactions tend to show that it is but a short step from hydrogen to water, and from carbon dioxide to monoxide, and *vice versa*, and that all of these must occur within the earth owing to the processes tending toward equilibrium. Whether hydrogen, in a particular case, occurs in the magmas in the free state, or in the form of water-gas, therefore becomes relatively unimportant. Because of this variation of state, the problem becomes more complex and broader in scope. For the most part, these water-gases are to be regarded as truly magmatic, and not derived from surface-waters penetrating to the liquid lavas, as will be brought out later. They are here put forward as essential factors in the evolution of the magmas from the original planetary matter.

The reactions working towards equilibrium are able to supply hydrogen and carbon monoxide under conditions favorable to their absorption and retention, even if they were not originally present as occluded gases. The sources of the gases obtained from rocks are so complex that it is difficult to determine how much is to be assigned to each. Because of the penetration of surface-waters containing carbonic acid in solution, throughout the accessible rocks of the earth's exterior, it is likely that, in many cases, the bulk of the gas obtained by heating powders in *vacuo* has been derived from acquired water and carbonated compounds. But in fresh meteorites, which presumably have not been subjected to action of this sort, occlusion is relatively more important.

From the constitution of meteorites, some of the principles of early terrestrial evolution may, perhaps, be inferred, though the growth of the



earth was probably not quite analogous, in all respects, to the formation of the meteorites. Whether we take the meteoritic material to represent the heavier part of the original matter of the solar system, or the stellar system, as a whole, matters little in the geologic problem. If, in truth, the unoxidized, heterogeneously aggregated material of meteorites be typical of the original heavy material of the earth, it becomes evident that, in the case of our planet, other factors have been at work which are not operative in the bodies of which the meteorites are supposed to be fragments. These visitors from space are characterized by such minerals as cohenite,  $(\text{Fe}, \text{Ni}, \text{Co})_3\text{C}$ , lawrencite,  $\text{FeCl}_2$ , oldhamite,  $\text{CaS}_2$ , and schreibersite,  $(\text{Fe}, \text{Ni}, \text{Co})_3\text{P}$ , which, next to nickel-iron, is the most widely distributed constituent of iron meteorites,<sup>1</sup> though of less importance in the stony specimens. Such compounds imply an absence of both free oxygen and water in notable quantities. Of like import is the absence of hydrated minerals, such as micas and amphiboles. Water and an oxygenated atmosphere appear to be the agents which are lacking in the bodies from which the meteorites were derived, but which have been the operative factors in working over the outer portion of the earth.

But the original source of the earth's atmosphere and hydrosphere is taken to be gas occluded, or absorbed, in the primitive meteoritic material. These original gases, escaping, furnished both atmosphere and hydrosphere when the earth became of sufficient size to retain them. A self-regulating system was inaugurated. In the early stages of the hydrosphere, when growth by infalling planetesimals was rapid, much water was buried within the fragmental crust. This material, worked over by volcanic activity, brought to the surface and subjected to weathering and erosion, and buried beneath more material, has undergone assortment and alteration until the accessible rocks at the present time are very different from the meteoritic matter. Since the earth attained its growth and the infall of planetesimals slackened, much less water has penetrated to great depths below the surface. Post-Archean sedimentaries have not yet reached thicknesses sufficient to carry inclosed water down to the depths from which the lavas arise. Deep mines indicate that fractures and fissures do not convey water down to very great depths at the present time. If water does not penetrate so rapidly now, and hydration and carbonation are less effective, it is also probably true that subsiding vulcanism brings less gas to the surface.

It is essentially a system of balance. At the same time that water is being buried with sediment, its elements, hydrogen and oxygen, the latter in the form of the oxides of carbon, are exhaled from the earth's interior through volcanic outlets. But the system here suggested is very different from the postulated limited cycle of underground water which, following Daubrée's famous experiment,<sup>2</sup> has crept into geologic literature as the origin of volcanic vapors and the *modus operandi* of vulcanism. Instead of surface-waters following cracks and fissures down to the hot lavas there to be absorbed, the water already is present, and is a part of the rocks and

<sup>1</sup> Farrington, *Jour. of Geol.*, vol. 9, pp. 405-407 and 525-526.

<sup>2</sup> Daubrée, *Études Synthétiques de Géologie Expérimentale*, t. 1, pp. 236-246.

magmas in the interior, whether actually combined as water, or as its elements held in solution, or chemically united in other compounds. These gaseous elements form an integral part in the magmas, having been vital factors in their development from the primitive planetary matter. That this process of reworking has gone on to considerable depths, if we are to start with typical meteoritic material, is evidenced by the fact that the deep-seated plutonic rocks are characterized by micas and other hydrous minerals, while mineral species of the meteoritic type are absent.<sup>1</sup>

The more restrictive phase of the problem of water will be discussed under the head of vulcanism.

### VULCANISM.

In the actual dynamics of vulcanism, provided the gases are original in the magmas, the state in which they occur is not of vital importance, except in so far as it determines the conditions under which the gases become free, from occluded or chemical bonds, to perform their part in the mobility of lavas, in the explosions which sometimes accompany eruptions, and in the phenomena of fumaroles and volcanic vents. The distinction between cavity, occluded, and chemically united gas, which is made in the case of solid igneous rocks, can not be extended to the liquid lavas. In the liquid lava the gas may be supposed to be imprisoned mechanically, or else to form a part of the magmatic solution. On the solidification of the mass, the gas, formerly existing in the free state, may enter chemical combinations at the lower temperature, may be occluded by the solid rock, or may become entrapped within the minerals last to crystallize. So, too, it is possible that some of the gas dissolved in the magma may, because of cooling and crystallization of adjacent portions of the solution, reach a supersaturated condition and appear in the solid rock also as gas inclusions. Otherwise, it would pass into the solid rock occluded or chemically combined. The condition of the gases examined in the laboratory need not, necessarily, correspond to a particular state of occurrence in the lava before crystallization.

Gases mechanically distributed throughout the lava would always be an operative factor in vulcanism, while such gases as were chemically combined in the solution would, presumably, only become free, and hence fully operative, upon the lowering of the temperature and the relief of pressure,<sup>2</sup> and probably but partially then. Since vapors and gases in the free state are the cause of volcanic explosions, they can be traced as far down in the conduits as explosions occur. From the nature of these explosions, which appear to be due to the accumulation of vapor gradually working upward until suddenly able to relieve itself, it is fair to suppose that

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<sup>1</sup> This statement should perhaps be qualified. The basalt at Ovivak, Greenland, contains iron strongly resembling the meteoric metal, and in which the minerals cohenite, lawrencite, and doubtfully schreibersite have been recognized. The occurrence of this terrestrial iron would indicate that material of this sort still occurs at points within the outer part of the earth.

<sup>2</sup> A falling temperature favors the liberation of hydrogen from water by ferrous compounds (see p. 67), while carbonates are most easily decomposed at low pressures (see p. 49).

aqueous vapor and the auxiliary gases are present in the free state at still greater depths.

It has been the observation of those who have studied volcanic eruptions that water-vapor is by far the most abundant of the gaseous products of volcanoes. Water is also the principal compound of the element hydrogen, which is quantitatively the most important gas obtained by heating igneous rocks in vacuo. According to one of the common theories of vulcanism, it is water, circulating underground and necessarily dissolving and absorbing mineral and gaseous material, which penetrates to the lavas and gives to them their supply of vapor and gases. Water, then, is a critical element in the theories of vulcanism, and likely to be a decisive factor, upon the basis of which many of these theories may stand or fall. It is, therefore, of great importance to know whether the aqueous vapor, which is so copiously exhaled from volcanic vents and plays such a rôle in vulcanism, is derived originally from the magmas, or is merely underground water which has been incorporated by the lava in its journey upward. A decision of this question will carry with it the solution of the allied question concerning the ultimate source of the other gases, and also throw much light upon some of the more comprehensive theories of vulcanism.

Appealing to the fact that chlorine, in the form of hydrochloric acid and volatilized chlorides, is one of the products of volcanoes, one of the standard hypotheses attributes the cause of vulcanism to the penetration of sea-water to the heated interior. If this were so, isolated volcanoes far out at sea would be expected to yield much more chlorine than those on the continents. But the Hawaiian volcanoes exhale comparatively little chlorine or sublimed chlorides. It has been claimed that rain-water, sinking into the cone, would have sufficient head to exclude the sea-water from the neighborhood of the hot lava. Rain, however, falls upon but a small part of the whole cone, whose greater portion is under the sea. It would seem that if rain-water, falling upon a cone built up from the ocean bottom, is able, by means of its head, to keep out the sea-water which covers the lower slopes, the same amount of water precipitated upon a continental volcano would be even more efficient in preventing the general underground water from coming in contact with the lava in the conduit. Whatever may be the reason for the small amount of chlorine given off by the volcanoes of Hawaii, sea-water does not reach the heated lavas in sufficient quantities to affect them appreciably.

On account of the pressure exceeding the crushing strength of the rock, pores and crevices can not exist at depths greater than 30,000 feet according to the most generous estimate,<sup>1</sup> and it is probable that continuous cracks cease much short of this. Beyond this extreme figure, meteoric waters can not be regarded as of any quantitative importance, on account of the extreme slowness of diffusion through solid bodies not containing minute fractures. Liquid carbon dioxide still existing under great pressure in sand grains of Pre-Cambrian age is a concrete example of this slowness. While, theoretically, water may extend downward to the limit of the zone of fracture, the testimony of deep mining appears to show that

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<sup>1</sup> Hoskins, 16th Ann. Rept. U. S. Geol. Surv., p. 853.



meteoric waters grow relatively scant, as a rule, below the uppermost 1,500 to 1,800 feet of the earth's crust.<sup>1</sup> This shallowness of meteoric water increases the difficulties encountered by the hypothesis that the lava beds are supplied from this source, since they rise from far greater depths and only the upper portions of their conduits would be exposed to these waters.

It is in this portion of the zone of fracture that Daubrée's much quoted experiment upon the Strasbourg sandstone<sup>2</sup> finds its application, if anywhere, since numerous capillary pores with plenty of water are requisites for the operation of this principle. This famous experiment demonstrated that, owing to its force of capillarity, boiling water will pass through a disk of sandstone, 2 centimeters in thickness, against a slight steam-pressure on the other side. But it was only necessary for the steam-pressure to reach 685 millimeters, or nine-tenths of an atmosphere, in order to prevent any more water from passing through the sandstone. It is a long jump from this trivial capillary force, equal to less than one atmosphere of steam-pressure, to the great pressures which would have to be overcome in the depths of the earth's crust in order to reach the hot lavas, even though it be allowed that the water-vapor, if it came in contact with the lava, would be absorbed. Capillary force seems quantitatively inadequate.

To reach the critical pressure of water due to the hydrostatic column, it is necessary to penetrate the earth to a depth of about 6,900 feet. At depths less than this, water passing into the vaporous condition, in the neighborhood of hot volcanic conduits, at temperatures below the critical point, should leave behind more or less of the matter held by it in solution, since the condensation, and hence molecular attraction of the vapor for solutes, is less than that of the water. Thus even if vapor from underground waters should enter the lavas, as Daubrée has suggested, in the outer 6,900 feet of the earth's crust, much of the chlorides, sulphates, carbonates, and silicates, dissolved in the water, would have been left behind. At depths between 6,900 feet and 25,000 feet, beyond which water can not penetrate, owing to the closure of all pores by the pressure of superincumbent rock, mineral matter dissolved in the water would probably still remain in solution when the liquid passed into the gaseous state at the critical temperature, since the density of the gas is equal to, or greater than, that of the liquid.

The lava, being under considerable pressure, may be supposed to occupy all the cracks and crevices in the adjacent rocks, except those of capillary dimensions. If, therefore, in the passage of underground water into vapor, preparatory to entering lavas in the outer 6,900 feet of the earth's crust, much of the dissolved mineral matter be deposited in the minute pores leading to the lava, they should quickly become sealed, preventing any further access, even of water, to the lava. To test this principle experimentally, a cylinder of medium-grained Potsdam sandstone from Wisconsin, 40 millimeters in diameter and 28 millimeters in thickness, was soldered into a short piece of iron piping, fitted at one end with an elbow

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<sup>1</sup> Kemp, *Economic Geol.*, vol. 2 (1907), p. 3; Finch, *Proc. Col. Sci. Soc.*, vol. 7 (1904), pp. 193-252.

<sup>2</sup> Daubrée, *Études Synthétiques*, t. 1, pp. 236-246.



to serve as a receptacle for water, and at the other with a cork and a condenser. When ready, the receptacle was filled with Lake Michigan water and a Bunsen burner was placed so as to heat the sandstone cylinder within the iron tube. One side of the sandstone was thus kept at a temperature slightly above  $100^{\circ}$ , while the other face, in contact with the water, remained just at the boiling-point. Water was found to penetrate the porous cylinder readily, evaporating and leaving its dissolved material within the mass of the sandstone, and escaping as steam on the farther side. The rate at which the water passed through the sandstone at the outset was not determined, but after 5 liters of lake water had been used, it was found that 129 cubic centimeters traversed the rock and were condensed in one hour. The rate slowly fell as the experiment progressed. While the thirteenth liter was being used, only 73 cubic centimeters passed through the sandstone per hour. It was evident that the pores were becoming clogged, but to complete the experiment with Lake Michigan water, which contains only 150 parts of solid matter per million, would have required too much time. To hasten the process, a saturated solution of calcium sulphate was substituted. This soon caused a marked slackening of the passage of water through the rock, and doubtless would have sealed the pores completely, if allowed sufficient time.

From this experiment, it appears certain that water, evaporating in the pore spaces of a rock and escaping as steam, will leave behind whatever material is in solution, until the crevices become clogged and the penetration of water ceases. This principle may be applied to the outer 6,900 feet of the earth's crust; in the superficial portion of this zone it should be very effective, since the conditions more nearly approach those of the experiment; in the lower portion of this belt, as 6,900 feet and the critical pressure (as well as temperature in the neighborhood of hot volcanic pipes) is approached, the density, and hence the solvent powers, of the water-vapor approach those of the liquid. The vapor, also, should escape less readily from the liquid at these depths, since the expansive force of the vapor drives the water back along its path with more difficulty. Toward the critical point of water, therefore, the application of this principle becomes more uncertain, but it would seem to be operative also at these depths, though more and more slowly as the critical point is neared.

It might be objected that the passage of water into vapor, involving the latent heat of steam, would keep the adjacent rocks cool and cause the deposition to take place at the very contact where the hot lava could fuse, and dissolve, the precipitated salts. But it is very doubtful whether the vaporization of such a small quantity of water, taking place with the slowness imposed upon it by the minuteness of the capillary pores, would keep the contact rocks at a temperature below  $365^{\circ}$ . The gap between  $365^{\circ}$  and  $1100^{\circ}$  is too great for there not to be a space, if of a few inches only, at an intermediate temperature. It is also to be remembered that the latent heat of steam diminishes with the pressure until, at the critical point, it becomes zero. The testimony of the country rocks through which a volcanic conduit has passed is that metamorphism has usually progressed to some distance from the contact of igneous intrusion. In a long-established volcano, where the rocks surrounding the conduit have

been heated to high temperatures, the deposition of the solutes from any penetrating water should have sealed the capillary tubes and fissures at a distance from the lava such that the latter cannot absorb them and keep the water-way open. Kemp has stated in a recent paper<sup>1</sup> that at the contacts with eruptives, limestone rocks, instead of being porous, are prevailingly dense and compact, and often very hard to drill, as if due to deposition within their interstices. However, the author assigned this supposed deposition to magmatic waters from the intrusion. This brings up a widely established view that magmas, instead of absorbing water from the intruded rocks, give it off, depositing matter in solution to form veins in the zone of fracture.

To quote Van Hise:<sup>2</sup>

In the belt of cementation, in consequence of the porosity of that zone, the material of the magma, both by direct injection and by transmission through water, may profoundly affect the average chemical composition of the intruded rock for great distances from the intrusive mass.

Geikie cites a case in Bohemia, where certain Senonian marls, invaded by a mass of Tertiary dolerite, begin to get darker in color and harder in texture at a distance of 800 meters from the contact, while, as the intrusive mass is approached, the interstratified beds of sandstone have been indurated to the compactness of quartzite.<sup>3</sup>

But considering only meteoric waters at depths greater than 6,900 feet, where water remains liquid up to the critical temperature, it is less probable that the pore spaces will be filled up in this manner. Nor does it seem likely that Daubrée's theory that water may penetrate rocks against a steam-pressure can operate at these depths, since that principle is dependent upon a marked difference between the capillarity of water and of steam, while at the critical point, the density of water-gas being the same as that of water, this force should be absent. The problem then becomes a question of equilibrium between the hydrostatic column of water and that of the lava, in which the pressure of the lava at a depth of 7,000 feet should be in the neighborhood of 2.7 times that of the water, though this preponderance steadily diminishes as the water-gas becomes condensed, with increasing depth, at a rate higher than lava. Whether under these conditions lava can absorb water-gas, is an open question.

Water can only penetrate from 25,000 to 30,000 feet below the surface on account of the closure of all crevices by pressure. But on the assumption that the temperature gradient in the outer part of the earth's crust is 1° C. for each 100 feet of descent (which is probably too high) the critical temperature will not be reached, except in the neighborhood of volcanic intrusions, until at a depth of about 36,000 feet. Hence, over the greater part of the earth, water will remain in the liquid state as far down as fractures and fissures will allow it to seep, and no appeal can be made to the more rapid and potent gaseous diffusion to carry it beyond 30,000 feet. But because of their heat, lavas must originate at much greater depths below the surface, and hence far beyond the reach of surface-waters, which can

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<sup>1</sup> Kemp, *Economic Geol.*, vol. 2, p. 11.

<sup>2</sup> Van Hise, *Monograph 47*, U. S. G. S., p. 714.

<sup>3</sup> Hibsche, cited by Geikie, *Textbook of Geology*, vol. 2, p. 774.

only come in contact with them, and only doubtfully then, in a very limited portion of the throat of the volcano.

These considerations seem to indicate that, for the most part, the volcanic gases and vapors have not been supplied to the lavas by ground waters, but are original constituents of the magmas. Doubtless at the beginning of an eruption, following a period of quiescence, much of the steam merely comes from such rain-water as may have accumulated in the crater and upper part of the cone, but this does not account for the gaseous emanations from the lava itself, nor from those volcanoes, such as Stromboli, and the well-known Solfatara near Naples, which maintain a mild form of eruption for long periods. Such meteoric water could contribute to the volcanic gases little except some dissolved air, together with a trace of carbon dioxide, and perhaps hydrogen from chemical action. Such soluble salts as this water might dissolve from the crater walls were brought up from the interior in the first place (making some allowance, however, for weathering), and so have little bearing on the case.

The hypothesis that the gases and vapors are originally from the magmas, is greatly strengthened by the volcanic activity in the moon, if, as is rather generally believed, the great pits on the surface of the moon are craters produced by volcanic explosions; if not, of course the argument does not hold. The gases and vapors which caused the tremendous outbursts can not be ascribed to the penetration of surface-waters and gases, for the moon has neither appreciable atmosphere nor hydrosphere, and, according to Stoney's doctrine, never could have held either, owing to its feeble gravitative control. Such gases as are implied by these explosions must be supposed to have arisen from within the interior of the moon. The extent of this explosive lunar vulcanism, in the absence of any appreciable atmosphere or hydrosphere, furnishes a strong argument against the belief that surface-waters and atmospheric gases are essential factors in terrestrial vulcanism.

Thus far evidence of a negative nature has been brought forward to show the difficulties in the way of thinking that surface-waters play a prominent rôle in volcanic phenomena. But more positive evidence can be presented to support the view that the hydrogen and water in the deep-seated rocks are truly magmatic. Micas are prominent constituents of the plutonic rocks. The immense granitic bathyliths, which were probably formed beyond the reach of ground-waters, are characterized by this group of minerals. In fact, micas are more abundant in the deep-seated rocks than in the surface lavas of similar composition. Yet all micas contain hydrogen (or hydroxyl) and yield water upon ignition. This varies with the mineral species and locality, ranging up to 4 or 5 per cent. If these micas in the massive intrusions are primary minerals, as they seem to be, and were out of the reach of ground-waters until long after they were crystallized, there appears no other alternative than to consider this hydrogen as inherent in the magma itself. The general petrological principle that plutonic rocks are micaceous and hornblendic, while their more superficial equivalents are more frequently characterized by pyroxenes which are less hydrous, may point toward the suggestion that the magmas originally contain considerable water or the elements which can produce it, but as



they approach the surface much of the hydrogen and water-vapor escapes and pyroxene minerals crystallize instead of these hydrous micas.

All of these facts and deductions lead to the general conclusion that our surface-waters have been derived from the interior of the earth, and oppose the idea that to explain the presence of hydrogen, or water, in magmas and rocks, we have merely to appeal to the penetration of surface-waters. The meteoric waters are limited to their superficial place and function, both in the evolution of magmas and in vulcanism; an ultimate source is found for these waters; and a steady supply of water and gases is furnished to the earth to offset the loss of vapor into space, and thus contributes to the globe one of the factors necessary to a long period of habitability for living organisms.

#### VOLCANIC GASES.

The gases which escape from fumarolic vents are in many respects similar to those obtained by heating igneous rocks in vacuo, but with the addition of oxygen and vapors of chlorides, fluorides, boric acid, and other high-temperature volatilizations. Though nitrogen is much more conspicuous in the analyses of volcanic gases than in those from rocks, this is doubtless due, in the main, to a mixture with atmospheric air. However, the greater heat of the volcano would also favor a higher proportion of nitrogen, as shown by my experiment. Much of the oxygen also is probably from the air. But an analysis of gas escaping from a stream of lava flowing on the sea bottom at Santorin gave Fouqué: oxygen, 21.11 per cent; nitrogen, 21.90 per cent; and hydrogen, 56.70 per cent.<sup>1</sup> This would suggest that the dissociation of water also contributes free oxygen.

Fouqué's studies at Santorin confirm the law of variation in composition of volcanic gases, first established by Sainte-Claire Deville,<sup>2</sup> namely, that the nature of the gas evolved depends upon the phase of volcanic activity. Hydrochloric acid, with free chlorine and fluorine, is given off only from the hottest fumaroles where the heat is sufficient to liberate these gases from chlorides and fluorides. At less active vents, sulphur dioxide is the most noticeable of the corrosive gases, while the cooler fumaroles exhale chiefly hydrogen sulphide, carbon dioxide, and nitrogen. Carbon dioxide and nitrogen escape from all the fumaroles. Fouqué found that the relative importance of hydrogen increased with rise of temperature, and that his marsh-gas (which, owing to an imperfection in the method of analysis in 1867, may have been carbon monoxide, or a mixture of carbon monoxide and marsh-gas) diminished as the activity increased. These observations are entirely in accord with the results of my differential temperature experiments with rock powders. Hydrogen sulphide and carbon dioxide are the gases expelled from the rocks at the lowest temperatures; carbon monoxide and marsh-gas appear at intermediate temperatures, while hydrogen is most prominent when the heat is carried to bright redness. Nitrogen is most abundantly liberated at red heat; hence the presence of that gas at the cooler vents and fissures is chiefly due to atmospheric air.

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<sup>1</sup> Fouqué, Santorin et ses Éruptions, p. 230.

<sup>2</sup> Sainte-Claire Deville, Ann. de Chim. et Phys., 52 (1858), p. 60.



While carbon dioxide escapes from all fumaroles in greater or less degree, it is at those vents whose activity has subsided beyond the point where hydrogen and the noxious gases are evolved that this gas is most conspicuous. For this reason, carbon dioxide has come to be regarded as marking the dying of the volcanic activity. A source for carbon dioxide after the disappearance of the other gases has been sought in the neighboring limestone formations, either from baking or from the chemical action of halogen or sulphur acids. The obvious difficulty confronting this conception is that limestone is not always present to furnish carbon dioxide. Experiments show that below  $400^{\circ}\text{C}$ . carbon dioxide is the principal gas evolved from rock material, and as the lava solidifying in the crater, or conduit, has not lost all its gas, it is only a part of the natural sequence of events that the escape of carbonic anhydride from the cooling lavas should continue for some time after the volcano has settled into quiescence. Some of this carbon dioxide doubtless also comes from previous lavas which, warmed again by the fresh lava, give up some of the carbon dioxide which my experiments show them to contain.

#### AMMONIUM CHLORIDE DEPOSITS.

Among the various substances which are deposited around fumaroles, sal-ammoniac, or ammonium chloride, is, in some respects, one of the most remarkable. Compounds of ammonium have not yet been recognized in igneous rocks, although rock powders often give off small quantities of ammonia gas when heated in vacuo. Chemical analyses of spring-waters report ammonium salts only in traces, such as may have been derived from the decay of organic matter. If ground-waters be, for the most part, unable to reach the lavas, even this rather doubtful source of ammonium compounds is not available. If the elements of the radical  $\text{NH}_4$  be supposed to have come from the interior magma, there are two alternative hypotheses still open. The first assumes that the radical  $\text{NH}_4$  existed intact in the magmatic solution in the form of ammonium salts and, volatilized by the heat upon the relief of pressure, gradually collected on the cooler portions of the crater. This hypothesis must, however, explain the apparent absence of these compounds in igneous rocks. The second believes that the ammonium chloride was formed synthetically in the throat of the volcano, from the nitrogen, hydrogen, and hydrochloric-acid gases. This would make it a direct product of volcanic gases.

The presence of ammonia, or its vaporized salts, in volcanic emanations leads to the formation of another interesting compound. Silvestri<sup>1</sup> has found iron nitride, as a lustrous metallic deposit, at a fumarole on Etna. This compound is due either to a reaction between the sublimed ferric chloride and free ammonia gas or to the ignition of the iron-bearing lava in the presence of ammonium chloride vapor. The appearance of iron nitride around fumaroles throws no direct light upon the question of its existence in the magmas, though it indirectly leads to the hypothesis that the nitrogen in the ammonia and its compounds came originally from iron nitride within the magma.

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<sup>1</sup> Silvestri, Pogg. Ann., vol. 157 (1876), pp. 165-172.

## SUBTERRANEAN GASES.

The atmosphere is now being fed by gases which escape through outlets other than those of active volcanoes. Work in the shafts of many deep mines in different parts of the world is often impeded by the exhalation of gases from the rocks. This is, of course, familiar in the case of organic rocks, such as coal, in which the decomposition of organic substances is in progress. Reference is here made especially to gases escaping from crystalline or other inorganic rocks. An exhalation of this kind is a notable phenomenon in several of the mines in the Cripple Creek region of Colorado, where nitrogen and carbon dioxide are poured into the workings in considerable quantities when the barometer is low.<sup>1</sup> Two analyses of the gas escaping into the Conundrum mine at Cripple Creek gave the following:

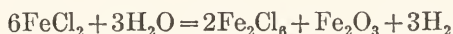
1st: Carbon dioxide, 10.2; oxygen, 5.7; nitrogen, 84.1; total, 100.

2d: Carbon dioxide, 8.3; oxygen, 10.2; nitrogen, 81.5; total, 100.

No carbon monoxide, marsh-gas, or hydrocarbons were detected.

The gas from the Elkton mine, which was analyzed by Dr. A. W. Browne, of Cornell University, consisted of nearly the same gases as from the Conundrum mine: Water-vapor, 1.4; carbon dioxide, 14.7; oxygen, 5.6; nitrogen, 76.8; argon, 1.5; total, 100.0. Hydrocarbons, methane, and hydrogen were absent.<sup>2</sup> The authors estimate that this gas may be considered to be 25 per cent of air, 59 per cent of nitrogen and argon, 15 per cent of carbon dioxide, and 1 per cent of water-vapor. The gas apparently is derived from greater depths than those at which it issues, since it is warmer than the air of the mines, and since practically no gas was encountered in the oxidized zone. They regard the outpouring as the last exhalation of the extinct volcano, around whose neck the Cripple Creek mines are located.

In some of the potash mines in the vicinity of Strassfurt trouble is caused by the escape of combustible gas into the workings. According to Precht,<sup>3</sup> blowers of this gas once lighted have burned continuously for periods as long as two months. An analysis of this gas by Precht shows it to be largely hydrogen. His figures are: Hydrogen, 93.05; methane, 0.778; carbon dioxide, 0.180; carbon monoxide, trace; oxygen, 0.185; nitrogen, 5.804; total, 100.002. This investigator believed that but little of the hydrogen could have come from the decomposition of organic matter; instead, he sought a source for it in the possible oxidation of ferrous chloride in the salt by water, according to the reaction:



This source of hydrogen is somewhat analogous to the production of the same gas by the action of water upon ferrous compounds at high temperatures, which has already been discussed, except that in the salt beds the supposed action has taken place at the ordinary underground temperature. But these gases coming from the sedimentary salt beds of the Upper Permian represent, of course, gas merely restored to the atmosphere, and not an original contribution to it.

<sup>1</sup> Lindgren and Ransome, Prof. Paper 54, U. S. G. S., pp. 252-270.

<sup>3</sup> H. Precht, Ber. Deutsch. Chem. Gesell., vol. 12 (1879), pp. 557-561.

<sup>2</sup> *Loc. cit.*

Nitrogen with an abnormal amount of inert gas (probably both argon and helium) occurs, under high pressure, in a gas-well at Dexter, Kansas.<sup>1</sup> However, instead of being derived from igneous rocks, this comes from a gas-bearing sand near the contact of the Permian with the Upper Carboniferous. An analysis of this gas gave:<sup>2</sup> Oxygen, 0.20; methane, 15.02; hydrogen, 0.80; nitrogen, 71.89; inert residue, 12.09; total, 100.

Neither carbon dioxide nor carbon monoxide was present in this gas. The methane, and perhaps the hydrogen also, may be attributed to the decomposition of organic matter, since natural gas-wells exist at no great distance away. But the remarkable feature of this analysis is the large amount of nitrogen with the very abnormal percentage of inert gas. From this analysis, and the testimony of many spring-waters which give off considerable quantities of argon and helium, it would appear that gases often collect underground somewhat in proportion to their chemical inertness. The chemically active gases apparently are more largely retained within the rocks by combination, while nitrogen, having less power to unite chemically, more largely escapes from the rocks and accumulates in reservoirs. Argon, still more inert than nitrogen, thus may reach such a high proportion as 12 per cent.

### GENERAL RELATIONS.

#### RELATIVE TO THE HYPOTHESIS OF A MOLTEN EARTH.

These studies show that, within the range of temperature employed, heat causes the expulsion of gases in whatever form they are held, and that the greater the degree of heat the more quickly and completely the gases are given off. There is reason to believe that this principle applies to the molten state as well as to the solid condition. If it be applicable to liquid lavas, it would favor the belief that a molten globe would have boiled out most of its gaseous matter before solidifying. Gases near the surface should escape rapidly. It might, perhaps, on first thought, be held that, while much of the gas in the outer portion would be lost, that existing in the central part of the sphere would be retained and slowly recharge the peripheral portion after a crust had formed and prevented further escape; but the molten globe, by hypothesis, grew up gradually, and essentially every part was once superficial. Even to-day, in an essentially solid earth, there are movements of lava that bring up gases from unknown depths, and it is reasonable to suppose that the molten sphere was stirred up by still more effective convection currents which facilitated the expulsion of gases and vapors, and that almost all of the gaseous material of the globe would have been boiled out before solidification set in.

The complete validity of this view depends much upon the fate of the gases after they have reached the surface. If they were retained in the form of a dense atmosphere, a condition of pressure-equilibrium might be established between the atmosphere and the gases in the liquid earth, by means of which the latter would retain some appreciable amount of gas. But if, as some believe, our atmosphere is about all that the earth

<sup>1</sup> Haworth and McFarland, *Science*, vol. 21 (1905), pp. 191-193.

<sup>2</sup> *Loc. cit.*



can control,<sup>1</sup> the gas expelled from the molten sphere in excess of the mass of the present atmosphere would escape and be lost to the planet. Geological evidences—early Cambrian glaciation, Paleozoic periods of aridity, and the general testimony of life—all point toward the conclusion that early terrestrial atmospheric conditions were not radically different from those of to-day. If the hypothesis of a heavy atmosphere be not permissible, it becomes very difficult to explain the presence of original gases and gas-producing compounds in plutonic rocks on the basis of the Laplacian or other hypotheses that postulate original fluidity.

#### RELATIVE TO THE PLANETESIMAL HYPOTHESIS.

After the gaseous matter of the ancestral sun was shot out from the solar surface to form the two arms of the spiral nebula, as postulated by the planetesimal hypothesis, the rock-producing portion is supposed either to have aggregated into planetesimal bodies, or to have been gathered, molecule by molecule, into the nucleus of the earth. The planetesimal bodies gathered in gas molecules of the atmospheric class both by chemical union and by surface adhesion or occlusion. As the earth grew by sweeping in the planetesimals, whatever gases they contained became entrapped in the body of the growing planet and well distributed throughout its mass. At first, the gravity of the earth may possibly have been able to hold only the gases brought in by planetesimal aggregates of rock material and those that became impounded in it by impact, but at a later stage, when increased mass enabled it to hold gaseous molecules, gases may have been added to the atmosphere directly from the nebula, and these, by chemical reactions, may have become united with the surface rocks. As soon as vulcanism commenced, a system of exchange was set up. While gases were being fed to the atmosphere by volcanic action, water, carbon dioxide, oxygen, and nitrogen were being buried with the surface rock material, partly by chemical union and partly by mechanical entrapment, as the growth by infalling matter continued. It is thus quite easy to understand how the earth came to be affected by these gases throughout its mass, and how they came to exist there in all available forms of retention.

While the carbon monoxide and methane derived from rocks by heating in vacuo are doubtless chiefly produced from the carbon dioxide and water present in the rock material, there seems good reason to suppose that similar reactions took place within the earth, as the surface material became buried and heated, and hence that carbon monoxide and methane exist, as such, in the earth's body, and are to be reckoned among the natural gases of the rocks.

#### RELATIVE TO ATMOSPHERIC SUPPLY.

The fact that many of the igneous rocks are able to yield hydrogen from reactions between water and ferrous compounds, at high temperatures, indicates that the material of the earth's crust is in a condition of partial oxidation only. Near the center of the earth there is probably very little oxygen, and even up to the surface, barring the weathered

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<sup>1</sup> R. H. McKee, *Science*, vol. 23 (1906), pp. 271-274.



mantle, the rocks are suboxidized. Yet the earth is surrounded by an oxygenated atmosphere. Since oxygen is not developed in the combustion-tube, and does not appear to exist as a free gas in igneous rocks, it is not likely that this constituent of the atmosphere has come directly as an exudation from the interior of the globe. It is to be sought, rather, in a dissociation or decomposition of compound gases by physical or organic agencies. Originally, enough oxygen was derived from water-vapor, by physical means, to permit the beginning of plant life; after vegetation appeared, an abundant source of oxygen was found in the carbon dioxide.

The average gas content of igneous rocks, as determined by the analyses now made, may be used to test the competence of the rocks to yield the present atmosphere. Taking the average volume of nitrogen per volume of rock to be 0.05, which is probably nearer the truth than the figure 0.09 given in table 16<sup>1</sup> (owing to leakage of air), it would require the liberation of all the nitrogen in the outermost 70 miles of the earth's crust to produce the nitrogen in the present atmosphere. For an estimate of the amount of igneous rock necessary to yield the carbon dioxide which is now locked up in limestone and coal deposits, we may take Dana's figure of 50 atmospheres of this gas, and an average of 2.16 volumes of carbon dioxide per volume of rock. To produce these 50 atmospheres of carbon dioxide, it is found that a thickness of 66 miles of crust would have to be deprived of its carbon dioxide<sup>2</sup>—a figure which corresponds fairly well with the estimate for nitrogen. If the water of the rocks be placed at 2.3 per cent, a depth of 70 miles would supply the hydrosphere.

On the planetesimal hypothesis, gas has been supplied from the interior to the atmosphere ever since an early stage of the earth's growth, probably from the earliest stage at which an atmosphere could be held, which may be placed at the time when the earth's radius was about 2,000 miles. From this it appears that only a small fraction of the full gas-producing possibilities of the rocks of the earth was required to supply the atmosphere. The fact that gases are still being given forth through volcanoes, and that the ejected lavas still have gas-producing qualities, makes it clear that all the resources of the interior are not yet exhausted. The working qualities of the planetesimal hypothesis, therefore, do not seem to be found wanting in either past possibilities of supply, present output, or prospective reserve.

### ACKNOWLEDGMENTS.

In conclusion, I wish to express my special thanks to Dr. Julius Stieglitz for constant advice in the conduct of the chemical researches; to Dr. Oskar Eckstein for much valuable assistance in the laboratory; to Dr. R. A. Millikan for helpful suggestions pertaining to physical principles and the designing of new pieces of apparatus; and to my father, Dr. T. C. Chamberlin, for proposing the investigation, and for constant sympathy and criticism during the progress of the work.

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<sup>1</sup> Ante, p. 28.

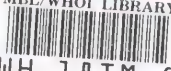
<sup>2</sup> The limestones, of course, are not here included.





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